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The Chemistry of Naphthenic Acids in Crude Oil Processing

Occurrence, Industrial Utilization, and the Role of Nuclear Magnetic Resonance Spectroscopy in the Analysis, Production, and Purification of Naphthenic Acid Streams

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Abstract

Naphthenic acids constitute the dominant acidic fraction of crude petroleum and represent one of the most consequential and least tractable compound classes encountered in refining and production operations. The term is applied, by long convention rather than by strict chemical definition, to the whole population of carboxylic acids indigenous to crude oil, a population that spans acyclic branched acids, mono- through hexacyclic saturated ring acids, aromatic and heteroatomic acids, polyfunctional oxygenated species, and the C_{80}–C_{82} isoprenoid tetraprotic 'ARN' acids responsible for calcium naphthenate deposition. This chemical heterogeneity is the origin of both the industrial problems these acids cause and the analytical difficulty they present. The economic consequences are direct: high-temperature naphthenic acid corrosion constrains the crude slate a refinery may safely process, metal naphthenate soaps and deposits disrupt upstream separation trains, interfacial activity stabilizes water-in-oil emulsions that resist desalting, and residual acidity degrades product quality and poisons downstream catalysts. Conversely, the same acids recovered from refinery caustic streams support a commercial trade in metal carboxylates used as paint and ink driers, polymerization and cure catalysts, rubber-to-metal adhesion promoters, wood preservatives, corrosion inhibitors, and lubricant additives, and this trade imposes its own analytical requirements on acid value, water, phenolic contamination, and unsaponifiable neutral oil content.

This white paper reviews the molecular chemistry, physical behavior, industrial impact, recovery, purification, and commercial application of naphthenic acids, and then examines in detail the analytical role of nuclear magnetic resonance spectroscopy across that entire chain. The central analytical argument developed here is that the capabilities of NMR spectroscopy and of ultra-high-resolution mass spectrometry are complementary rather than competitive. Mass spectrometry resolves elemental composition and hydrogen deficiency at the level of individual congeners but cannot, from mass alone, distinguish a saturated ring from an aromatic ring or from an olefinic double bond; NMR spectroscopy cannot resolve congeners at all but measures aromaticity, ring-junction methine content, branching, average chain length, and carbonyl speciation directly and quantitatively. A second argument, developed with explicit order-of-magnitude sensitivity calculations, is that direct observation of carboxyl functionality in whole crude oil is not achievable at industrially relevant acid numbers, since at a total acid number of 0.5 mg KOH g^{-1} the carboxyl proton represents approximately 7×10^{-5} of the total proton integral, whereas the same functionality in a recovered naphthenic acid concentrate represents several percent of the proton integral and is measured without difficulty. The practical consequences of this dichotomy are traced through the paper: whole-crude acidity is accessible to NMR only indirectly, through multivariate calibration, while isolated acid fractions and commercial naphthenic acid products are accessible to rigorous, standard-referenced quantitative NMR.

Quantification strategies are examined in detail, including direct quantitative ^{1}H and ^{13}C NMR with certified internal standards, methyl esterification followed by integration of the methoxyl singlet, ^{31}P phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, which resolves carboxylic, phenolic, and aliphatic hydroxyl functionality and water content in a single spectrum, and ^{19}F derivatization approaches for carbonyl speciation. The application of benchtop and on-line NMR at 43 to 100 MHz to process monitoring is then developed for the recovery and purification train specifically, covering feedstock screening, caustic extraction, acid springing, neutral oil removal, distillative fractionation, product quality control, and the manufacture of metal naphthenates. Chemometric prediction of total acid number from low-field ^{1}H NMR spectra is presented alongside a candid assessment of its limitations, and in particular of the correlative rather than causal basis of such models and the consequent risk of failure when a calibration is extrapolated to an unfamiliar crude slate. A critical assessment section identifies the specific technical vulnerabilities that a reviewer or an opposing technical expert would be expected to attack, and

recommended workflows are proposed for four common industrial scenarios. Sixty bibliographic sources supporting the discussion were verified through CrossRef before drafting.

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1. Introduction and Scope

Acidic constituents have been recognized in petroleum for more than a century, and the collective name applied to them — naphthenic acids — has survived largely unchanged despite a steady accumulation of evidence that the name describes an operational fraction rather than a chemical class. In current usage the term is applied to the whole population of carboxylic acids indigenous to crude oil, a population within which alicyclic acids are numerically dominant but by no means exclusive [1]. That looseness of definition is not a semantic inconvenience alone. It propagates into specification, into contract language, into corrosion prediction, and into the analytical methods by which the industry attempts to control these materials, and it accounts for a substantial fraction of the disagreement that arises when two laboratories report different naphthenic acid contents for the same sample.

The industrial significance of the class is twofold, and the two aspects pull in opposite directions. Within the refinery and the production facility, naphthenic acids are a liability. They drive high-temperature corrosion of transfer lines, furnace tubes, distillation column internals, and side-cut piping in the temperature window between roughly 200 and 400 °C [19,20]. They react with divalent cations at oil–water interfaces to form metal naphthenate deposits and soaps that foul separators and disrupt produced-water treatment [17,15]. They confer interfacial activity that stabilizes water-in-crude emulsions and impedes desalting [44]. Outside the refinery gate, however, the same acids recovered from spent caustic streams support an established specialty chemical trade whose principal products are the oil-soluble metal carboxylates used as coating driers, cure and polymerization catalysts, tire-cord adhesion promoters, wood preservatives, and lubricant and fuel additives. The refiner therefore has both an incentive to remove these acids and, where volumes justify it, an incentive to recover and sell them.

Analytical chemistry sits at the center of both problems. Purchase and blending decisions for opportunity crudes are made on the basis of acid number; asset-integrity decisions on metallurgy and inhibitor dosing are made on the basis of acid number and sulfur content; recovery-plant control and product release are made on the basis of acid value, water, and impurity content. Yet the primary industrial measurement, the total acid number determined by potentiometric titration, is a bulk neutralization number that responds to every acidic species present, including phenols, hydrogen sulfide, mercaptans, inorganic acids, and additive residues, and it therefore does not measure naphthenic acids [25,27]. The gap between what is measured and what actually matters is the space in which spectroscopic methods must operate.

This paper addresses that space with particular attention to nuclear magnetic resonance spectroscopy. The scope is deliberately wide, since the analytical requirements differ sharply along the value chain. Sections 2 and 3 develop the molecular and physicochemical description of the acids. Section 4 treats their behavior in crude production and refining, including corrosion, naphthenate deposition, emulsion stabilization, and the analytical basis of the acid number. Section 5 describes recovery and purification, and Section 6 describes commercial applications and the specification parameters those applications impose. Sections 7 through 9 constitute the analytical core of the paper: the NMR observables available for naphthenic acid systems, the quantification strategies that exploit them, and the deployment of benchtop and on-line NMR for process monitoring and control. Section 10 places NMR alongside the orthogonal techniques with which it must be combined, and Section 11 states plainly where NMR fails and where published NMR-based claims are most vulnerable to technical challenge. Section 12 proposes concrete workflows for four recurring industrial scenarios.

2. Definition, Nomenclature, and Molecular Architecture

2.1 The $C_nH_{2n+Z}O_2$ Formalism and Its Limits

The classical description of naphthenic acids expresses their composition through the general formula $C_nH_{2n+Z}O_2$, in which n is the carbon number and Z is a zero or negative even integer expressing hydrogen deficiency relative to the corresponding acyclic saturated acid [1]. Within the simplifying assumption that all hydrogen deficiency arises from saturated ring closure, the absolute value of Z divided by two returns the number of rings, so that Z = 0 describes acyclic acids, Z = −2 monocyclic acids, Z = −4 bicyclic acids, and so on through the fused polycyclic series. Carbon numbers from approximately seven to thirty are commonly reported for the classical fraction, with molecular weights concentrated between roughly two hundred and five hundred daltons, although both the carbon-number range and the molecular-weight distribution shift substantially with crude source and with the boiling range of the cut examined [1,3].

The convenience of the formalism conceals a serious ambiguity, and that ambiguity is central to the analytical argument of this paper. Hydrogen deficiency is a count of rings plus double bonds, not a count of rings. A Z value of −12 is satisfied equally by an acid bearing six fused saturated rings, by an acid bearing one benzene ring and two saturated rings, and by an acid bearing a naphthalene nucleus and a single alicyclic ring, since an aromatic ring contributes four degrees of unsaturation. Mass spectrometry, however exquisite its resolving power, returns elemental composition and therefore returns Z; it does not by itself distinguish these possibilities. Any statement about ring count derived from Z alone is a statement conditioned on an assumption of full saturation, and that assumption is demonstrably false for a substantial fraction of the acid population in many crudes [2,3]. Nuclear magnetic resonance measures aromatic and aliphatic hydrogen and carbon directly and therefore resolves the ambiguity that the formalism creates. This complementarity is developed in Section 7.

2.2 Classical Monoprotic Acids

The numerically dominant structures within the classical fraction are monocarboxylic acids in which the carboxyl group is attached, most often through a short alkyl tether rather than directly, to a saturated ring system built from fused cyclopentane and cyclohexane units. Alkyl substitution on those rings is extensive and the acyclic members of the family are strongly branched, a feature that distinguishes them clearly from the straight-chain fatty acids of biological origin and that is consistent with their formation by the microbial oxidation of petroleum hydrocarbons rather than by direct inheritance of biolipids [1,4]. The structural work of Seifert and Teeter established by isolation, derivatization, and mass spectrometry that polycyclic naphthenic, monoaromatic, and diaromatic carboxylic acids are all genuine constituents of crude petroleum rather than artifacts of isolation, and that finding has been repeatedly confirmed by later ultra-high-resolution mass spectrometry [2,5].

2.3 Aromatic, Heteroatomic, and Polyoxygenated Species

Modern negative-ion electrospray Fourier transform ion cyclotron resonance mass spectrometry has demonstrated that the acid fraction of a heavy crude comprises thousands of distinct elemental compositions, distributed across O_2 species and a substantial population of O_3 through O_6 species, along with acids containing nitrogen, sulfur, or both [5,3]. The polyoxygenated compounds include hydroxy acids, keto acids, and dicarboxylic and higher polycarboxylic acids, and they are frequently under-represented in analytical schemes calibrated on commercial naphthenic acid preparations, since the commercial materials derive from distillate caustic extraction and are therefore biased toward the lower-boiling monoprotic

fraction. Sulfur-containing acids merit specific attention in the corrosion context because they couple the two principal high-temperature degradation mechanisms operating in the crude unit.

Terminology has evolved accordingly. In environmental practice the broader designation naphthenic acid fraction compounds is now widely preferred, precisely to signal that the acid-extractable organic fraction is not restricted to the classical $C_nH_{2n+z}O_2$ series [7,9]. The same caution is warranted in refining practice, and any specification or contract clause referring simply to naphthenic acid content should state the analytical method by which that content is defined.

2.4 The ARN Tetraprotic Acids

A distinct and industrially critical subclass was identified in the mid-2000s in connection with calcium naphthenate deposition. These are tetraprotic acids of approximately C_{80} carbon number and molecular mass near 1230 daltons, designated ARN acids, whose skeleton consists of two biphytanyl diacid units joined through their C20 methyl positions and bearing four to eight cyclopentane rings. The structure was determined by high-field NMR spectroscopy in combination with mass spectrometry, and homologues bearing additional methyl substitution at C_{81} and C_{82} were subsequently characterized by the same approach [10,11]. The skeletal architecture is closely related to archaeal biphytanyl ether lipids, which supports a biological rather than diagenetic origin for this subclass.

The industrial importance of these species is out of all proportion to their concentration. Tetraprotic functionality permits each molecule to bridge multiple divalent cations, so that reaction with calcium at an oil–water interface produces a cross-linked, gel-like polymeric salt rather than a simple soap. The resulting deposit is adherent, hardens on exposure to air, and accumulates in separators, hydrocyclones, and produced-water systems [15,17]. Concentrations in the parts-per-million range within the crude are sufficient to generate operationally significant deposition, which places the analytical requirement in a very different regime from bulk acid number determination and effectively excludes direct NMR observation in the whole crude. Analytical determination of ARN content in petroleum has therefore relied on selective extraction followed by high-temperature gas chromatography, high-performance liquid chromatography, or mass spectrometry [12,13,14], with NMR reserved for structure elucidation on isolated material and for confirmation of deposit composition.

2.5 Geochemical Origin

Naphthenic acids in the classical sense are principally the products of in-reservoir biodegradation. Systematic comparison of biodegraded and non-biodegraded oils from common source rocks demonstrates that total acidity and the abundance of carboxylic acids increase markedly with biodegradation level, that acyclic acids are removed preferentially at moderate biodegradation levels, and that the surviving population becomes progressively enriched in polycyclic species as degradation advances [4]. This origin explains several observations of practical importance: the association of high acid numbers with heavy, low-API, biodegraded crudes; the correlation of acid content with elevated concentrations of naturally occurring metals; and the tendency for acidity to concentrate in the heavier distillation cuts, since the acid population shifts toward higher molecular weight as biodegradation proceeds.

3. Physicochemical Properties Relevant to Processing

3.1 Acidity, Dimerization, and Solution Behavior

Naphthenic acids behave as ordinary weak carboxylic acids in aqueous solution, with dissociation constants clustered in the region characteristic of aliphatic carboxylic acids. In a hydrocarbon matrix, however, the dominant solution behavior is not dissociation but hydrogen-bonded dimerization, since the carboxyl group forms a strong cyclic dimer in nonpolar media. This dimer equilibrium is the immediate reason why the carboxyl proton resonance in a nonpolar solvent is broad, strongly concentration-dependent, and strongly temperature-dependent, and why direct integration of that resonance is unreliable as a quantitative measure. The same equilibrium governs infrared practice, where the monomer and dimer carbonyl bands are separately resolved and both must be accounted for in quantitative work [27].

Partitioning between oil and water phases is governed by molecular weight, by ring content, and above all by pH, and the partition coefficient of the undissociated acid differs from that of the carboxylate by several orders of magnitude. Systematic partitioning studies on both commercial naphthenic acid mixtures and crude-oil-extracted acids show that the effective distribution is a composition-weighted average over a broad congener population, so that the apparent partition coefficient of a mixture drifts as extraction proceeds and the lighter, more water-favoring members are depleted first [16]. This behavior is directly relevant to the design and control of caustic extraction, since a single-stage measurement of extraction efficiency will not extrapolate reliably to a multistage cascade.

3.2 Interfacial Activity and Emulsion Stabilization

The combination of a polar head group and a bulky, oil-soluble alicyclic tail makes naphthenic acids intrinsically surface-active, and their contribution to the stabilization of water-in-crude emulsions is well documented. Interfacial behavior is markedly pH-sensitive, since the ionized carboxylate is far more surface-active than the neutral acid, and it is further modified by the presence of divalent cations, which convert an adsorbed monolayer into a cross-linked interfacial film. Comparative study of commercial and indigenous naphthenic acids using ^{1}H NMR, diffusion-ordered spectroscopy, rheometry, pendant-drop tensiometry, and gas chromatography–mass spectrometry has shown that the indigenous material contains larger molecular species with correspondingly smaller diffusion coefficients, and that this difference in molecular size translates into different interfacial adsorption and desorption kinetics [44]. The practical implication is that laboratory studies conducted with a commercial naphthenic acid surrogate may not reproduce the behavior of the indigenous acids in the crude of interest, and any conclusion drawn from a surrogate should be qualified accordingly.

3.3 Metal Salt Formation

Reaction with metal cations yields naphthenates whose properties depend strongly on the cation. Monovalent sodium and potassium naphthenates are soaps: water-soluble at sufficient pH, strongly emulsifying, and responsible for the viscous soap emulsions that disrupt produced-water treatment. Divalent calcium naphthenate is the deposit-forming species, and where tetraprotic ARN acids are present the deposit is a cross-linked network rather than a simple salt [15,17]. Field mitigation strategies exploit the pH dependence directly, most commonly through injection of a low-molecular-weight organic acid such as acetic acid to suppress ionization of the naphthenic acids and thereby prevent naphthenate formation, a strategy whose effectiveness and limitations have been assessed in field practice [18].

In the commercial context the same chemistry is the product. Metal naphthenates of cobalt, manganese, zirconium, calcium, zinc, copper, lead, and iron are manufactured deliberately by fusion or by double decomposition, and the oil solubility that makes calcium naphthenate a fouling problem upstream is precisely the property that makes cobalt naphthenate a useful drier in an alkyd coating.

3.4 Thermal Behavior and Volatility

Naphthenic acids recovered from refinery streams distill over a broad range, and commercial grades are separated by vacuum distillation into cuts of differing average molecular weight and acid value. Thermal decarboxylation becomes significant at elevated temperature and constitutes both a nuisance and an opportunity: a nuisance because it liberates carbon dioxide and generates ketones and other neutral products that contaminate distillate cuts, and an opportunity because catalytic decarboxylation over basic oxides is a viable deacidification route for high acid crudes [58]. Ketone formation has been demonstrated directly in open-system corrosion testing of naphthenic acids, where Fourier transform ion cyclotron resonance mass spectrometry identified the ketone products formed under conditions representative of the refinery corrosion environment [22]. The analytical consequence is that a thermally stressed sample is not compositionally identical to the sample charged, and NMR carbonyl-region analysis will show ketone and ester resonances alongside carboxyl resonances in such material.

4. Naphthenic Acids in Crude Production and Refining

4.1 Acid Number: What Is Actually Measured

The industrial currency of crude acidity is the total acid number, expressed as milligrams of potassium hydroxide required to neutralize one gram of sample. The reference determination is potentiometric titration in a titration solvent with alcoholic potassium hydroxide, in which the inflection points of the electrode potential curve define the endpoints [25]. Catalytic thermometric titration provides an alternative endpoint detection principle that is less sensitive to electrode fouling in dark and viscous crude matrices and has been adopted where potentiometric endpoints are indistinct [26].

Neither method is selective. The measured neutralization number aggregates carboxylic acids, phenols, hydrogen sulfide and mercaptans, inorganic acids carried over from upstream chemical treatment, and any acidic additive residues present. Two crudes of identical total acid number may therefore differ substantially in carboxylic acid content and, more importantly, in corrosivity. Recognition of this limitation motivated development of a naphthenic acid number determined by mid-infrared spectroscopy through the carbonyl absorption characteristic of the carboxyl group, which responds to the carboxylic fraction specifically and can be reported alongside the titrimetric total acid number to expose the non-carboxylic contribution [27]. Chemometric prediction of the total acid number from attenuated total reflectance infrared spectra has likewise been demonstrated for a Colombian crude population [28]. The distinction between a neutralization number and a carboxyl content is fundamental to the analytical argument of this paper and is returned to in Section 8.2, where an NMR-based spectroscopic acid value is proposed as a second independent measure.

4.2 High-Temperature Naphthenic Acid Corrosion

Naphthenic acid corrosion is a nonaqueous, high-temperature degradation mechanism whose essential feature is the formation of an oil-soluble iron carboxylate. Iron is attacked with liberation of hydrogen and formation of iron naphthenate, which dissolves in the flowing hydrocarbon rather than depositing as a protective scale, so that fresh metal is continuously exposed. Attack is characteristically localized,

appearing as sharp-edged grooving and pitting in regions of high wall shear stress, and is concentrated in the temperature window of roughly 200 to 400 °C where the acids are both mobile and volatile enough to reach the metal surface but not yet extensively decarboxylated [19,20,23]. The affected assets are predictable: furnace tubes and transfer lines, atmospheric and vacuum column internals, side-cut piping, and heat-exchanger tubes handling heavy vacuum gas oil, which frequently carries the highest acid number of any cut.

The mechanism cannot be treated in isolation from sulfidation, since the two operate simultaneously in almost every real crude. Sulfur species generate iron sulfide scale, which is adherent and can be protective; naphthenic acids both attack the metal directly and dissolve the sulfide scale, and the sulfide can in turn regenerate free acid from the iron carboxylate. The balance between the two determines whether a protective inner scale survives. Detailed mechanistic study has shown that corrosion rate in the combined regime is governed by solid-state diffusion of iron through the inner scale and by the surface kinetics on that scale, rather than by the simple sum of two independent attack processes [21]. The corollary for prediction is uncomfortable but important: corrosion rate is not a function of acid number alone, and correlation of observed corrosion with total acid number across a population of crudes of differing sulfur content should be expected to be poor.

Mitigation is accordingly multi-layered. Metallurgical upgrade to molybdenum-bearing austenitic stainless steels is the durable answer for the most severely exposed components; crude blending to hold the acid number of the charge below an operating threshold is the most common commercial answer; high-temperature phosphorus-based filming inhibitors are used where metallurgy cannot be changed; and chemical deacidification of the crude or of specific cuts is applied where the economics support it. All of these strategies depend on timely, reliable measurement of the acidity of the charge and of individual cuts, which is precisely where rapid spectroscopic methods become operationally valuable.

4.3 Metal Naphthenate Deposition and Soap Emulsions

In upstream production, the encounter of naphthenic acids with formation water containing calcium and other divalent cations produces the deposition problems described in Section 2.4. Two distinct failure modes are recognized and require different responses. Calcium naphthenate deposition, associated with the tetraprotic ARN acids, produces hard adherent solids on separator internals and in produced-water systems. Sodium naphthenate soap formation, associated with the classical monoprotic acids at elevated pH, produces stable viscous emulsions and interface pads rather than solids. Diagnosis of which mechanism is operating is a prerequisite to selecting a treatment, and misdiagnosis is common because both present initially as separation upset [17]. Deposit forensics accordingly matters: the presence of C_{80} tetraacids in a recovered deposit is diagnostic, and their determination in deposits and in petroleum has been addressed by chromatographic and mass spectrometric methods [13,14], with NMR providing the definitive structural confirmation on isolated material [10,11].

4.4 Emulsion Stabilization and Desalting

The surface activity described in Section 3.2 has a direct operational cost in the desalter. Acid-stabilized water-in-crude emulsions resist coalescence, carry salt and sediment forward into the crude unit, and increase the chloride load on the overhead system. Because the stabilizing mechanism is interfacial rather than bulk, the diagnostic measurements that matter are the water content, the droplet size distribution, and the interfacial film properties, none of which is accessible from acid number. Low-field NMR is unusually well suited to two of these three. Water content and droplet size distribution in water-in-crude emulsions are routinely determined by relaxation and pulsed field gradient diffusion measurement, and the pulsed field

gradient with diffusion editing approach was developed specifically to separate the restricted-diffusion signature of dispersed water droplets from the bulk oil signal in an optically opaque emulsion [45,46]. This capability links directly to the process monitoring discussion in Section 9.4.

4.5 Product Quality and Downstream Consequences

Residual acidity is a specification issue in its own right for several products, and it carries consequences beyond the specification. Acidic species contribute to instability and color formation in distillate fuels, they promote water pickup and emulsion formation in lubricant base stocks, and calcium associated with naphthenate chemistry acts as a poison for hydrotreating and fluid catalytic cracking catalysts and shortens delayed coker furnace run lengths. Deacidification of specific cuts by catalytic esterification is therefore practiced as an alternative to whole-crude treatment, with esterification of the naphthenic acids to the corresponding esters providing acid-number reduction without the high temperatures required for decarboxylation [59,60]. Esterification is also, as Section 8.2 develops, the basis of one of the most useful NMR quantification strategies available for these materials, so that the process chemistry and the analytical chemistry converge on the same reaction.

5. Recovery, Purification, and Commercial Grades

5.1 Caustic Extraction from Distillate Streams

Commercial naphthenic acids are not extracted from whole crude. They are recovered as a by-product of the caustic treatment applied to straight-run distillate streams, principally kerosene, jet fuel, and light and heavy gas oils, in which sodium hydroxide is contacted with the hydrocarbon to remove acidic species and thereby meet acidity, corrosion, and stability specifications on the finished distillate. The naphthenic acids transfer to the aqueous phase as sodium naphthenates, and the resulting spent caustic solution carries them together with cresylic acids, sulfides, mercaptides, and entrained hydrocarbon. The composition of this stream is therefore set by the refinery's own distillate treating requirements rather than by the acid recovery objective, which is the principal reason that commercial naphthenic acid quality varies with refinery source and with crude slate.

Extraction efficiency depends on caustic strength, contact stage design, temperature, and the molecular-weight distribution of the acids present. Because the higher-molecular-weight acids partition less favorably into the aqueous phase, the recovered material is systematically biased toward the lighter members of the population relative to the acids present in the crude, and the reported partitioning behavior of both commercial mixtures and crude-extracted acids confirms this compositional shift [16]. Any attempt to use a commercial naphthenic acid as an analytical calibrant for whole-crude acidity inherits that bias, which is a recurring and under-acknowledged source of error in quantitative work.

5.2 Springing

Recovery of the free acid from the naphthenate-bearing caustic proceeds by acidulation, universally termed springing in the trade, in which mineral acid — most commonly sulfuric acid — is added to lower the pH below the point at which the carboxylate is protonated. The liberated acids separate as an organic phase and are decanted or centrifugally separated from the aqueous brine. The stream at this point is crude naphthenic acid: dark, viscous, wet, and contaminated with entrained hydrocarbon, residual sulfur species, phenolic acids, and inorganic salts. Control of the springing step is a pH and interface-management problem, and

incomplete springing leaves valuable acid in the brine while over-acidification increases downstream neutralization and corrosion duty [24].

5.3 Neutral Oil Removal, Dehydration, and Distillative Refining

The crude naphthenic acid is then upgraded through a sequence whose objective is the removal of everything that is not carboxylic acid. Water is removed by flashing or by vacuum dehydration. Entrained hydrocarbon — the neutral oil or unsaponifiable fraction — is the most consequential impurity, because it dilutes the acid without contributing to acid value and therefore directly determines the achievable product grade. It is removed by a combination of flashing, solvent treatment, and vacuum distillation. Final fractionation under vacuum then separates the acids into cuts differentiated by boiling range, and hence by average molecular weight, average ring content, and acid value. Color bodies and residual sulfur compounds are addressed by adsorptive or chemical treatment where a light-colored product is required.

The quality parameters that define a commercial grade follow directly from this sequence, and they are summarized in Table 1 together with the analytical technique conventionally applied to each and the NMR observable, where one exists, that carries the same information. The final column of that table anticipates the analytical development in Sections 7 through 9 and is intended as a working map from process objective to measurement.

Table 1. Quality parameters of recovered naphthenic acid products, the conventional determination, and the corresponding NMR observable. Entries marked as proposed are put forward in this paper as methodologically sound but not, to the author's knowledge, established as standardized industrial practice, and require validation before adoption.

Quality parameter	Process origin	Conventional determination	NMR observable
Acid value (mg KOH g^{-1})	Set by feed cut and by neutral oil removal efficiency	Potentiometric or color-indicator titration	^{31}P integral of phosphitylated COOH against internal standard; or methoxyl singlet after esterification (both quantitative)
Neutral oil / unsaponifiables	Hydrocarbon co-extracted with the acids and incompletely stripped	Saponification and solvent extraction, gravimetric	Difference between total aliphatic ^{1}H integral and the acid-associated proton population; proposed as a direct spectroscopic estimate (Section 8.2)
Water content	Residual from springing and washing	Karl Fischer titration	Hydroxylated-TMDP resonance near 132 ppm in the ^{31}P experiment, measured in the same acquisition as acid value
Phenolic (cresylic) acids	Co-extracted into caustic from the same distillate	Chromatographic or wet-chemical separation	^{31}P resonances in the 145–137 ppm region, cleanly resolved from carboxylic OH at 136–134 ppm
Average molecular weight / ring content	Set by the vacuum distillation cut point	Vapor pressure osmometry; boiling range distribution	Average molecular parameters from combined ^{1}H and ^{13}C integration with elemental analysis
Aromatic content	Crude source and cut dependent	Chromatographic group type analysis	Aromatic ^{1}H region (6.0–9.3 ppm) and aromatic ^{13}C region (100–160 ppm), directly integrated

Quality parameter	Process origin	Conventional determination	NMR observable
Color	Thermal history, sulfur and nitrogen species	Visual or instrumental color scale	No direct NMR observable
Sulfur content	Carryover of sulfidic and mercaptide species	Elemental analysis, X-ray fluorescence	No routine NMR observable at typical concentrations

5.4 Deacidification as an Alternative to Recovery

Where recovery is not economic, the refiner's objective is destruction or transfer of the acids rather than their isolation. The available routes divide into destructive and non-destructive categories. Non-destructive routes include neutralization, solvent extraction, adsorption, and ion exchange, and share the disadvantage of generating an aqueous or solid waste stream and, frequently, of promoting emulsions. Destructive routes include thermal and catalytic decarboxylation, typically over basic oxides such as magnesium oxide, which is effective but requires temperatures above about 250 °C where the corrosion problem is itself aggravated [58], and catalytic esterification, which achieves substantial acid-number reduction at considerably lower temperature and has been demonstrated for diesel fuel and for whole acidic crude in fixed-bed continuous-flow configuration [59,60]. Extraction with organic amines, coupled with structural characterization of the recovered acid fraction by infrared spectroscopy, NMR, and high-resolution mass spectrometry, has also been developed for high acid crudes [42]. Each route requires reliable acid-number monitoring on both feed and product to establish conversion, and the residence times involved in continuous-flow operation make an at-line or on-line measurement considerably more useful than an off-line titration.

6. Industrial Uses and Applications

6.1 Metal Naphthenates as Driers and Catalysts

The principal commercial destination of recovered naphthenic acid is conversion to oil-soluble metal carboxylates. The utility of the naphthenate anion in this role rests on three properties: the bulky, irregular, highly branched alicyclic structure suppresses crystallization and confers excellent solubility in hydrocarbon and in drying-oil media; the carboxylate binds a wide range of metals in a form that remains soluble; and the material is liquid or readily soluble at ambient temperature, which simplifies formulation.

In surface coatings, cobalt, manganese, zirconium, calcium, and zinc naphthenates function as driers, catalyzing the autoxidative cross-linking of alkyd and other oxidatively curing binders. Cobalt acts principally as a surface drier through its redox cycling in the hydroperoxide decomposition sequence, while zirconium and calcium function as through-driers and auxiliary driers. In unsaturated polyester and vinyl ester thermosets, cobalt naphthenate is the classical accelerator used with peroxide initiators. In rubber compounding, cobalt naphthenate and related cobalt carboxylates promote adhesion between brass-plated steel cord and the rubber matrix in tire construction. Each of these applications specifies the product not by naphthenic acid content but by metal content, and product quality control therefore centers on metal assay, solubility, viscosity, and freedom from insolubles — with the acid value of the feed acid determining the achievable metal loading.

6.2 Wood Preservation and Biocidal Uses

Copper naphthenate is a long-established wood preservative used for the protection of poles, posts, ties, and fabricated timber against fungal decay and insect attack, applied by pressure treatment and by non-pressure

dip, brush, and spray methods, and used for remedial treatment of in-service structures. Zinc naphthenate serves a related role where a lighter-colored, lower-toxicity treatment is required. The oil solubility of the naphthenate is central to performance because it governs penetration into the wood substrate.

6.3 Additive, Inhibitor, and Surfactant Applications

Beyond driers and preservatives, naphthenic acids and their derivatives serve as extreme-pressure and antiwear components in lubricating oils and greases, as fuel additives, as emulsifiers and demulsifiers, as defoamers, and as intermediates in the manufacture of amine-based corrosion inhibitors for oilfield and refinery service. The last of these is a notable circularity: acids removed from a refinery stream because they cause corrosion are converted into amine salts and imidazolines that are injected elsewhere to prevent it. Naphthenic acids are also employed as metal extractants and phase-transfer agents in hydrometallurgical separations, again exploiting the combination of a coordinating carboxylate with a strongly oil-soluble tail.

6.4 Environmental and Regulatory Context

Because naphthenic acids are both produced deliberately and released incidentally, their environmental behavior is subject to sustained regulatory and scientific attention, most prominently in connection with oil sands process-affected water, where the acid-extractable organic fraction is the principal toxicological concern. The analytical literature developed for that context — covering isolation, characterization by ultra-high-resolution mass spectrometry, and the persistent difficulty of quantifying a compositionally undefined mixture against an arbitrary commercial calibrant — is directly transferable to industrial analytical practice and is among the most methodologically rigorous body of work on these materials [7,8,9]. The identification of individual acids within such mixtures by combined chromatographic and spectrometric methods has demonstrated both what is achievable and how much analytical effort individual-congener identification demands [8]. That effort is not available in a process control context, which is the argument for bulk-average spectroscopic methods.

7. Nuclear Magnetic Resonance Spectroscopy of Naphthenic Acid Systems

7.1 The Case for NMR and Its Complementarity with Mass Spectrometry

Nuclear magnetic resonance spectroscopy occupies a position in naphthenic acid analysis that is frequently misunderstood, and the misunderstanding runs in both directions. NMR is sometimes promoted as an alternative to mass spectrometry for compositional characterization, which it is not, and it is sometimes dismissed as insensitive and uninformative for complex mixtures, which is equally wrong. The correct statement is that the two techniques measure different things and that neither substitutes for the other.

Ultra-high-resolution mass spectrometry, and particularly negative-ion electrospray Fourier transform ion cyclotron resonance, resolves the acid population into thousands of individual elemental compositions and reports each as a carbon number and a hydrogen deficiency [5,6,7]. This is a level of compositional detail that NMR cannot approach and will never approach, because the acid population contains thousands of structurally similar molecules whose resonances superimpose into broad, featureless envelopes. What mass spectrometry does not deliver, however, is the partition of hydrogen deficiency between saturated rings, aromatic rings, and olefinic unsaturation, since all three contribute identically to the mass defect. Nor does it deliver ionization-independent quantitation, since electrospray response varies with structure across the population and the resulting distributions are semi-quantitative unless calibrated congener by congener.

NMR delivers precisely what mass spectrometry does not. The proton and carbon spectra partition the sample directly into aromatic and aliphatic pools, resolve methyl from methylene from methine, distinguish carbons alpha to a carbonyl from those remote from it, and provide integrals that are, under properly configured acquisition conditions, strictly proportional to the number of nuclei present and independent of chemical structure. That last property is the decisive one: an NMR integral requires no response factor. The natural analytical architecture is therefore joint, with mass spectrometry supplying the congener distribution and NMR supplying the aromaticity, branching, and average structural parameters that convert that distribution into a defensible structural picture. Published work on thermally degraded petroleum has used exactly this combination, characterizing solid-phase and liquid–liquid extracted acid fractions by ^{1}H NMR alongside negative-ion FT-ICR mass spectrometry [41], and the monitoring of liquid–liquid extraction of naphthenic acids from Brazilian crude has been followed by the mass spectrometric arm of the same pairing [43].

7.2 ^{1}H NMR Observables

The proton spectrum of a petroleum acid fraction dissolved in deuterochloroform divides into regions whose boundaries are conventional rather than absolute, since the underlying resonances overlap continuously. The assignments in Table 2 follow the framework applied throughout petroleum NMR practice [29,34], with the addition of the carboxyl-specific features that concern the present subject. Two of the entries carry disproportionate analytical weight. The first is the region between approximately 2.1 and 2.6 ppm, which contains the protons on the carbon alpha to the carboxyl group. In an acyclic or tethered acid this is a methylene triplet near 2.35 ppm; in an acid bearing the carboxyl directly on a saturated ring it is a ring methine multiplet near 2.3 to 2.5 ppm, cyclohexanecarboxylic acid providing the reference case. This region unfortunately also contains benzylic protons alpha to an aromatic ring, so its use as an acid-specific measure requires either a low-aromaticity sample or independent determination of the aromatic content. The second is the region between roughly 3.4 and 4.0 ppm, which is essentially empty in hydrocarbon streams and which becomes the analytical window of choice once the acids are converted to their methyl esters, as developed in Section 8.2.

Table 2. Conventional ^{1}H NMR chemical shift regions for petroleum acid fractions in $CDCl_3$, with the structural assignment and the analytical significance of each region for naphthenic acid work.

δ (ppm)	Assignment	Analytical significance for naphthenic acids
0.5–1.0	Terminal CH_3; methyl in the γ position or further from an aromatic ring	Average alkyl chain length and degree of branching; used in the methyl hydrogen determination of ASTM D8383
1.0–1.5	CH_2 and CH in chains; naphthenic ring methylene remote from substitution	Dominant envelope; carries ring and chain population but is not resolvable into either alone
1.5–2.1	CH_2 and CH β to a carboxyl or to an aromatic ring; ring methylene adjacent to a substituted carbon	Partially diagnostic of substitution pattern on the alicyclic system
2.1–2.6	CH_2 and CH α to a carboxyl group; CH_3 and CH_2 α to an aromatic ring	The principal direct proton signature of carboxyl substitution; compromised by benzylic overlap in aromatic samples
3.4–4.0	Essentially vacant in untreated hydrocarbon streams; OCH_3 of methyl esters at 3.65–3.67 after derivatization	The analytical window for esterification-based quantification (Section 8.2)

δ (ppm)	Assignment	Analytical significance for naphthenic acids
6.0–9.3	Aromatic protons, monoaromatic through polynuclear	Direct measurement of aromaticity, which resolves the ring-versus-aromatic ambiguity in mass-spectrometric Z values
9.5–13.5	Carboxyl OH, broad and variable	Present but analytically unreliable; position and width depend on concentration, temperature, water content, and dimer equilibrium (Section 7.3)

7.3 The Carboxyl Proton: Why Direct Integration Fails

It is tempting to treat the carboxyl proton as the obvious analytical handle, since it is the functional group of interest and it resonates far downfield of everything else in a hydrocarbon spectrum. In practice it is among the least reliable observables available, and the reasons are worth stating explicitly because the temptation recurs.

The carboxyl proton is exchangeable. It exchanges with any water present in the sample or the solvent, with any alcohol or phenol present, and between acid molecules through the hydrogen-bonded dimer. The observed resonance is therefore a population-weighted exchange average whose chemical shift moves over a range of several parts per million with concentration, temperature, and water content, and whose linewidth is set by the exchange rate rather than by the intrinsic relaxation of the nucleus. In a wet sample the acid proton and the water proton coalesce into a single broad feature of no analytical value whatsoever. Even in a rigorously dried sample the resonance is broad, sits on a curved baseline in the region where residual protio-solvent and spinning sidebands often appear, and is easily lost to aggressive baseline correction. Its integral is further biased by incomplete relaxation, since a broad exchange-averaged line has a short apparent transverse relaxation time but its longitudinal relaxation may nonetheless be long. Section 8.1 shows that in whole crude oil the resonance is in any case far below the practical detection threshold, which settles the question for that matrix. In a concentrated acid product the resonance is readily visible, but even there its integral should be regarded as a qualitative confirmation of carboxyl presence rather than as a quantitative measure, and the derivatization routes of Section 8 should be used for quantification.

7.4 ^{13}C NMR Observables

Carbon-13 spectroscopy is the more structurally informative of the two common nuclei for this class of material, at the cost of sensitivity and of substantially more demanding quantitative conditions. The carbonyl region is diagnostic and, importantly, resolves the carbonyl functionalities from one another: aliphatic and alicyclic carboxylic acid carbonyls appear near 180 to 184 ppm, aromatic carboxylic acid carbonyls near 170 to 173 ppm, esters near 172 to 175 ppm, and ketones, which are formed both by thermal decarboxylation and by the corrosion reaction itself, near 205 to 215 ppm [22]. A single carbon spectrum therefore establishes whether the oxygenate population of a stressed or processed sample is still carboxylic or has begun to convert to neutral products, which no titration can do.

Table 3. ^{13}C NMR chemical shift regions of analytical importance for naphthenic acid systems in $CDCl_3$.

δ (ppm)	Assignment	Comment
205–215	Ketone carbonyl	Marker of thermal decarboxylation and of the naphthenic acid corrosion reaction pathway
178–185	Carboxylic acid carbonyl, aliphatic and	Diagnostic of the classical naphthenic acid population; non-

δ (ppm)	Assignment	Comment
	alicyclic	protonated, therefore long T_1 and no nuclear Overhauser enhancement
170–176	Aromatic carboxylic acid and ester carbonyl	Esters appear here after derivatization or after catalytic esterification treatment
100–160	Aromatic and olefinic carbon	Basis of the aromatic carbon determination of ASTM D5292
50–55	OCH_3 of methyl esters (51.4–51.9)	Confirms completeness of esterification; complements the ^1H methoxyl integral
34–48	Carbon α to the carboxyl group; ring methine at a substituted ring junction	Ring-substituted acids place this carbon near 43 ppm; chain-tethered acids near 34 ppm
22–33	Chain and ring methylene	Dominant aliphatic envelope
10–22	Terminal and branch methyl	Chain-length and branching information

Quantitative carbon acquisition demands conditions that are routinely neglected. The carboxyl carbon is not protonated, so it experiences no useful nuclear Overhauser enhancement and relaxes slowly; longitudinal relaxation times of the order of ten to twenty seconds are ordinary. Inverse-gated proton decoupling must be used to suppress the differential Overhauser enhancement that would otherwise inflate protonated-carbon integrals relative to the carbonyl, and a paramagnetic relaxation agent, conventionally chromium(III) acetylacetonate at concentrations in the range of a few tens of millimolar, should be added to shorten and equalize the relaxation times. Recycle delays must then be set from measured relaxation times on the actual matrix rather than from a textbook default. Where these conditions are not met, the carbonyl integral is systematically low, frequently by tens of percent, and any acid content derived from it is correspondingly wrong. This is the single most common technical defect in published quantitative carbon work on petroleum fractions and it is the first thing a competent reviewer will check.

7.5 Average Molecular Parameters

The most productive use of combined proton and carbon spectroscopy on an isolated acid fraction is the calculation of average molecular parameters: aromaticity, average number of aromatic and naphthenic rings, average alkyl substituent length, degree of substitution of the aromatic system, and average molecular weight when the spectroscopy is combined with elemental analysis and an independent molecular weight determination. The methodology is well established for heavy crude fractions and vacuum residues [34,35] and transfers directly to naphthenic acid concentrates, with the carboxyl group entering the bookkeeping as an additional known structural unit whose abundance is fixed by the acid value. Because the acid value provides an accurate, independently measured count of carboxyl groups per gram, the acid fraction is in fact a more tractable subject for average-structure analysis than a whole vacuum residue, where no comparable anchor exists.

A worked average-structure determination on a recovered naphthenic acid product yields, from a single pair of spectra and an elemental analysis, the average carbon number, the average number of rings, the fraction of those rings that are aromatic, the average number and length of alkyl substituents, and the average number of carboxyl groups per molecule. The last of these distinguishes a monoprotic product from one contaminated with polyprotic species and is not obtainable from acid value alone, since acid value reports equivalents per gram and cannot distinguish a low-molecular-weight monoacid from a high-molecular-weight diacid.

7.6 Two-Dimensional and Editing Experiments

Distortionless enhancement by polarization transfer and attached proton test experiments separate methyl, methylene, and methine carbons and are the fastest route to the ring-junction methine population that distinguishes fused polycyclic acids from monocyclic acids bearing long substituents. Heteronuclear single-quantum coherence spectroscopy disperses the crowded aliphatic envelope into two dimensions and permits the alpha-carbon correlation of the carboxyl-bearing carbon to be located even where the corresponding one-dimensional proton resonance is obscured by benzylic overlap. Heteronuclear multiple-bond correlation establishes the connectivity between the carboxyl carbon and the protons two and three bonds distant, which is the experiment that determines whether the carboxyl is attached directly to a ring or through a tether, and it is this class of experiment, applied to painstakingly isolated material, that established the ARN tetraacid structures [10,11].

These experiments are structure-elucidation tools, not process tools. Their place in naphthenic acid work is on isolated fractions, on deposit forensics, and on the characterization of reference materials, and their cost in instrument time places them firmly in the high-field laboratory rather than in the plant.

7.7 Relaxation and Diffusion Observables

Beyond the chemical-shift spectrum, the relaxation and diffusion behavior of these systems carries information that is directly relevant to the operational problems described in Section 4. Transverse relaxation time distributions in crude oils correlate with viscosity and density and have been developed extensively as a rapid characterization route [40,38]. Time-domain NMR has been applied to the reconstruction of petroleum distillation curves [39]. For emulsion problems specifically, pulsed field gradient diffusion measurement resolves the restricted diffusion of water confined within droplets from the free diffusion of the continuous oil phase and thereby returns a droplet size distribution in an opaque sample without dilution or optical access [45,46]. Diffusion-ordered spectroscopy applied to naphthenic acid samples themselves distinguishes molecular size populations and has been used to demonstrate that indigenous crude acids comprise larger species than commercial preparations [44]. Each of these observables is accessible on low-field, permanent-magnet hardware, which is what makes them candidates for plant deployment.

8. Quantification Strategies

8.1 The Sensitivity Problem, Stated Numerically

Any discussion of quantifying naphthenic acids by NMR should begin with an order-of-magnitude estimate of what is being asked, because the answer determines which strategies are viable and immediately disqualifies several that are periodically proposed. The calculation is elementary and is set out here explicitly so that it may be checked and adapted.

A total acid number of 0.5 mg KOH g^{-1} corresponds to 0.5 divided by 56.1, or 8.9 micromoles of titratable acid per gram of sample. A typical crude oil contains approximately 13 percent hydrogen by mass, which is 0.130 grams of hydrogen per gram of sample, or 129 millimoles of hydrogen per gram. If every titratable acid group carried one carboxyl proton, that proton population would represent 8.9×10^{-6} divided by 0.129, or 6.9×10^{-5} of the total proton inventory — sixty-nine parts per million of the total ^{1}H integral. Even at a total acid number of 3.0 mg KOH g^{-1}, which is a severely acidic crude, the carboxyl proton represents only about four hundred parts per million of the integral, and it appears as a broad exchange-averaged line rather than as a sharp resonance. Against a practical integration threshold of the order of one part per thousand for a well-resolved narrow line in a clean spectrum, and considerably worse for a broad line on a sloping

baseline, direct observation of the carboxyl proton in whole crude oil is not merely difficult but arithmetically excluded.

The carbon nucleus offers no relief. Taking a carbon content of approximately 85 percent by mass, a gram of crude contains about 70.8 millimoles of carbon, so at a total acid number of 0.5 mg KOH g^{-1} the carboxyl carbon represents 1.3×10^{-4} of the carbon inventory, or about one hundred and twenty-six parts per million of the ^{13}C integral, and it is a non-protonated carbon with a long relaxation time competing against a vast protonated aliphatic envelope. The conclusion is unavoidable and is the organizing principle of the remainder of this section: whole-crude acidity is not directly observable by NMR at industrially relevant acid numbers, and any NMR-based whole-crude acid number is therefore either an indirect chemometric correlation or the product of a chemical amplification step.

The situation in a recovered naphthenic acid product is entirely different, and the contrast is instructive. A product of acid value 230 mg KOH g^{-1} contains 4.10 millimoles of carboxyl per gram. At a hydrogen content near 11 percent by mass, the total proton inventory is about 109 millimoles per gram, so the carboxyl proton alone represents approximately 3.8 percent of the ^{1}H integral and the one or two protons on the alpha carbon represent a further four to eight percent. These are not marginal signals; they are among the larger resolved features in the spectrum. The same product converted to its methyl esters places three methoxyl protons per carboxyl in an otherwise vacant spectral window, amounting to roughly ten percent of the total proton integral. The practical rule that follows is that NMR quantification of naphthenic acids should be performed on the concentrate wherever the analytical question permits, and that where whole crude must be analyzed, the analysis should proceed either by extraction and concentration, by chemical derivatization into a favorable nucleus, or by frank acceptance that the result is a multivariate correlation rather than a measurement.

Table 4. Order-of-magnitude signal fraction for carboxyl-derived resonances across matrices of interest. Assumptions: crude oil taken as 13 wt% H and 85 wt% C; naphthenic acid concentrate taken as 11 wt% H; one titratable proton per equivalent. These figures are worked estimates intended to establish feasibility, not measured values.

Matrix and acidity	Carboxyl content (mmol g^{-1})	Observable	Approximate fraction of total integral
Crude oil, TAN 0.5 mg KOH g^{-1}	0.0089	COOH proton (broad)	7×10^{-5} (69 ppm) — not detectable
Crude oil, TAN 3.0 mg KOH g^{-1}	0.053	COOH proton (broad)	4×10^{-4} (414 ppm) — not reliably detectable
Crude oil, TAN 0.5 mg KOH g^{-1}	0.0089	Carboxyl ^{13}C (non-protonated)	1.3×10^{-4} (126 ppm) — not practical
Crude oil, TAN 3.0 mg KOH g^{-1}, esterified	0.053	OCH_3 singlet, 3 H per COOH, vacant window	1.2×10^{-3} — feasible at high field, marginal at 60 MHz
Crude oil, any TAN, phosphitylated	—	^{31}P of derivatized COOH	Not a fraction: the ^{31}P spectrum has no hydrocarbon background at all
Acid concentrate, AV 230 mg KOH g^{-1}	4.10	COOH proton	≈ 3.8 % — readily observed
Acid concentrate, AV 230 mg	4.10	α-CH_2 or α-CH at 2.1–2.6	≈ 4–8 % — readily integrated

Matrix and acidity	Carboxyl content (mmol g^{-1})	Observable	Approximate fraction of total integral
KOH g^{-1}		ppm	
Acid concentrate, AV 230 mg KOH g^{-1}, esterified	4.10	OCH_3 singlet at 3.65 ppm	≈ 10 % — the preferred quantitative handle

8.2 Esterification and the Spectroscopic Acid Value

Conversion of the carboxylic acids to their methyl esters transforms an intractable exchangeable proton into three chemically equivalent, non-exchangeable, sharp protons resonating as a singlet at 3.65 to 3.67 ppm in a spectral window that is essentially vacant in every petroleum stream that has not been contaminated with oxygenates. The corresponding ester methoxyl carbon appears near 51.4 to 51.9 ppm and provides an independent confirmation of derivatization completeness. The chemistry is standard, is the same chemistry practiced industrially for catalytic deacidification [59,60], and has been applied to petroleum acid fractions in the analytical literature in conjunction with proton NMR characterization of methylated fractions.

The quantitative procedure follows directly. The esterified sample is prepared gravimetrically with a certified internal standard of known purity, the spectrum is acquired under conditions that satisfy the requirements of quantitative proton NMR — adequate recycle delay relative to the longest longitudinal relaxation time in the sample, sufficient digital resolution, careful phase and baseline treatment, and integration limits set consistently [53,54] — and the molar carboxyl content is calculated from the methoxyl integral divided by three, referenced to the internal standard. Multiplication by 56.106 converts moles of carboxyl per gram into an acid value expressed in the familiar milligrams of potassium hydroxide per gram.

The quantity so obtained is proposed here as a *spectroscopic acid value*, and its analytical interest lies principally in what it does not include. Unlike a titration, it responds only to species bearing a derivatizable carboxyl group. Phenols do not form methyl esters under the mild conditions used, hydrogen sulfide and mercaptans do not contribute, and inorganic acidity does not contribute. The difference between the titrimetric total acid number and the spectroscopic acid value is therefore a direct measure of the non-carboxylic acidity of the sample, which is exactly the quantity that the naphthenic acid number determined by infrared spectroscopy was devised to isolate [27] and exactly the quantity that determines whether a total acid number should be expected to correlate with corrosivity. To the author's knowledge this specific comparison has not been established as a standardized industrial practice, and it is put forward here as a proposal warranting method development and validation rather than as an accepted technique.

Three practical cautions attach to the esterification route. Reagent selection matters: the derivatization must be quantitative under conditions mild enough to avoid transesterification of any glycerides present and to avoid attack on other functionality, and the completeness of conversion must be demonstrated on the actual matrix rather than assumed from model compound behavior. Residual methanol resonates near 3.49 ppm and is well separated at 300 MHz but only marginally separated at 60 MHz, where 0.16 ppm corresponds to under ten hertz; volatile reagent residues must therefore be removed before benchtop measurement. Finally, samples containing fatty acid methyl esters from biodiesel blending will show a methoxyl singlet before any derivatization is performed, and a blank spectrum is mandatory. Silylation, which places nine trimethylsilyl protons per carboxyl near 0.3 ppm in a window that is likewise vacant in petroleum, offers a threefold sensitivity advantage over methylation and is worth evaluating, but excess silylating reagent and its byproducts resonate in the same region and the derivatives are moisture-sensitive; this route is noted as a candidate rather than recommended.

8.3 ^{31}P Phosphitylation

The most powerful derivatization strategy available for this problem, and the one least exploited in petroleum practice, is phosphitylation followed by phosphorus-31 NMR. The reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane reacts with active hydrogen functionality — carboxylic acids, phenols, aliphatic alcohols, and water — to form phosphite esters whose phosphorus resonances are well dispersed and well resolved by functional class. The methodology was developed for lignin characterization [47,48] and has since been extended to biomass-derived oils, pyrolysis oils, and biocrudes [49,50,51].

The advantage for petroleum acid work is structural rather than incremental. Phosphorus-31 is one hundred percent naturally abundant and has a high gyromagnetic ratio, so its intrinsic sensitivity is favorable. More importantly, a hydrocarbon matrix contains no phosphorus, so the phosphorus spectrum of a phosphitylated crude oil contains signals only from derivatized functionality and from the reagent itself. The dynamic range problem that defeats direct proton and carbon observation, as quantified in Section 8.1, simply does not exist: the analyte is not a small signal on top of an enormous one, it is the only signal present. A crude of total acid number 1.0 mg KOH g^{-1} contains 17.8 micromoles of acid per gram, so a hundred-milligram sample in half a millilitre of solvent presents the derivatized acid at roughly three to four millimolar, a concentration that is comfortably measured by phosphorus NMR in a few hundred transients on a conventional high-field spectrometer.

Table 5. ^{31}P NMR resonance regions following derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, as established in the lignin and bio-oil literature and applicable to petroleum acid fractions.

δ (^{31}P, ppm)	Derivatized functionality	Relevance to naphthenic acid streams
≈ 175	Unreacted reagent	Its presence confirms that reagent was in excess and derivatization is complete; its absence invalidates the analysis
≈ 152 or ≈ 145	Internal standard (N-hydroxy-5-norbornene-2,3-dicarboximide or cholesterol respectively)	Quantitation reference; standard must be chosen to avoid overlap with sample resonances
150–145	Aliphatic hydroxyl	Alcohols and hydroxy acids; also flags glycol or alcohol process-chemical carryover
145–137	Phenolic hydroxyl	Cresylic acids co-extracted with naphthenic acids in refinery caustic — a direct product-quality measurement
136–134	Carboxylic hydroxyl	The naphthenic acid determination itself; long-chain and alicyclic acids cluster near 134.3–134.6 ppm
≈ 132.2	Hydroxylated reagent formed from water	Simultaneous water determination in the same acquisition, replacing a separate Karl Fischer measurement

Four constraints govern the transfer of this methodology from biomass to petroleum, and each requires experimental attention before the method is deployed. Solubility is the first: the derivatization is conventionally performed in a pyridine–chloroform mixture, and asphaltene precipitation from a heavy crude in that medium would remove an unknown fraction of the acid population from the measurement. Deasphalted oil or a maltene fraction may therefore be the appropriate analytical substrate for heavy crudes, with the consequence that the result applies to that substrate rather than to the whole crude. Water control is the second: water consumes reagent stoichiometrically and, while this is turned to advantage as a water determination, a wet sample requires a correspondingly larger reagent charge and an unrecognized water excess produces a silent under-determination of the acids. Thiol interference is the third: sulfhydryl

functionality is also phosphitylated, and in a mercaptan-bearing stream the resonance assignments must be established rather than assumed. Derivative stability is the fourth: the phosphite esters degrade over time in solution and the sensitivity of the determination to preparation, storage, and acquisition timing has been examined explicitly for biocrude matrices, with the conclusion that short and consistent handling protocols are essential [51]. Subject to these controls, phosphorus-31 phosphitylation is the author's recommended reference method for the carboxyl content of a naphthenic acid stream, and its ability to report carboxylic acid, phenolic acid, alcohol, and water content from a single spectrum makes it exceptionally efficient for product quality control on recovered naphthenic acids.

8.4 ^{19}F Derivatization

Fluorine-19 offers the same absence of matrix background as phosphorus-31 together with comparable sensitivity, and derivatization schemes based on fluorinated reagents have been developed for oxygenate characterization in complex biofuel matrices. Reaction of carbonyl functionality with 4-(trifluoromethyl)phenylhydrazine followed by fluorine-19 NMR has been established for the quantitative determination of aldehydes and ketones in bio-oils [52], and this specific chemistry is of interest in the naphthenic acid context not for the acids themselves but for the ketones formed during thermal decarboxylation and during the corrosion reaction [22,58]. For carboxyl determination the fluorine route offers no advantage over phosphitylation and carries the disadvantage that a suitable, quantitatively reacting fluorinated acylating or esterifying reagent must be selected and validated for this matrix. Fluorine-19 derivatization is therefore recommended here as a complement for carbonyl speciation in thermally stressed streams rather than as a primary acid determination.

8.5 Quantitative Practice and the Uncertainty Budget

Whichever observable is chosen, the credibility of the result rests on acquisition and processing practice that is frequently treated casually. The recycle delay must be set from measured longitudinal relaxation times on the actual sample, with the slowest-relaxing resonance of interest governing; for non-protonated carbonyl carbons and for phosphite esters this is not a trivial requirement. Nuclear Overhauser enhancement must be suppressed by inverse-gated decoupling in any heteronuclear quantitative experiment. Digital resolution must be sufficient that integration limits do not truncate the lineshape, and for broad lines the integration region must extend far enough into the wings to capture the Lorentzian tails. Phase and baseline correction must be applied conservatively, since aggressive polynomial baseline fitting will consume a broad minor resonance sitting on a curved background. The internal standard must be certified, must not overlap the analyte, must not react with the sample or the derivatizing reagent, and must be weighed on a balance whose calibration is traceable.

An honest uncertainty budget for a derivatization-based determination has at least five contributions: the gravimetric preparation of sample and standard, the purity assignment of the standard, the completeness of the derivatization reaction, the integration of the analyte and standard resonances, and the stability of the derivative over the interval between preparation and acquisition. The third and fifth of these are specific to derivatization methods and are the ones most often omitted from reported uncertainties. In a laboratory operating under ISO/IEC 17025, each must be estimated and documented, and the completeness of derivatization in particular should be demonstrated by a recovery experiment on a spiked matrix rather than inferred from the disappearance of a starting-material resonance.

9. NMR in Process Monitoring and Control

9.1 Instrument Classes and Their Proper Roles

Three classes of NMR instrumentation are relevant, and confusion between them accounts for a good deal of unrealistic expectation. Superconducting high-field spectrometers, operating from 300 MHz upward, deliver the chemical shift dispersion and sensitivity required for structure elucidation, average molecular parameter determination, two-dimensional experiments, and reference-method quantification. Cryogen-free permanent-magnet benchtop spectrometers, operating between roughly 43 and 100 MHz, deliver resolved chemical shift information at a small fraction of the cost and footprint and without cryogen logistics, and have matured into genuine analytical instruments over the past decade [55,56]. Time-domain relaxometers, operating typically between 2 and 25 MHz with no chemical shift resolution at all, deliver relaxation and diffusion measurements on optically opaque, multiphase samples.

The standards infrastructure reflects this division and demonstrates that NMR is not a novelty in petroleum practice but an established one. Aromatic carbon content by high-resolution NMR is standardized in ASTM D5292 [30], hydrogen content by low-resolution NMR in ASTM D4808 and D7171 [31,32], and methyl hydrogen content by high-resolution NMR in ASTM D8383 [33]. On-line and at-line deployment of NMR analyzers for refinery process control has a history extending to the 1990s, covering applications from alkylation and reforming control through gasoline and diesel blending to crude assay [29], and the acquisition parameter considerations specific to continuous-flow benchtop operation have been examined systematically [57].

9.2 Chemometric Prediction of Acid Number, and Its Limits

The most widely reported NMR route to crude acidity is multivariate calibration. Partial least squares regression of proton NMR spectra against reference acid numbers has been demonstrated at 60 MHz on a dataset of more than one hundred and seventy crude oils, alongside models for API gravity, sulfur content, and distillation yields, with external validation errors reported as comparable to the reproducibility of the reference ASTM methods [37]. Comparable multivariate work at higher field on neat crude samples has predicted a range of physical and chemical properties [36], and the analogous approach applied to attenuated total reflectance infrared spectra has been reported for Colombian crudes [28]. The engineering value of such models is real: a measurement returned in minutes on a neat sample, with no solvent and no titration, has obvious operational utility for tank certification, crude receipt, and blend control.

The interpretation of these models, however, requires care that is not always exercised, and the point is important enough to state without hedging. Section 8.1 established that at a total acid number of 0.5 to 3.0 mg KOH g^{-1} the carboxyl proton contributes between seventy and four hundred parts per million of the proton integral, as a broad exchange-averaged line. At 60 MHz that contribution is not merely below the integration threshold; it is below the noise of the individual spectrum for any realistic acquisition time. A partial least squares model predicting acid number from such a spectrum is therefore not measuring the acid. It is regressing acid number onto the bulk hydrogen distribution — aromaticity, mean chain length, branching index, naphthenic character — and it succeeds to the extent that acidity co-varies with those descriptors across the calibration population. That co-variance is genuine and geochemically well founded, since acidity is a product of biodegradation and biodegradation simultaneously depresses API gravity, raises aromaticity, and enriches polycyclic structures [4]. The model is a valid empirical correlation with a real physical basis. It is not a determination of carboxylic acid content.

Three practical consequences follow, and they define the boundary of safe use. First, the model will degrade or fail on any sample in which acidity has been decoupled from bulk composition: a partially deacidified

crude, a blend of a high-acid and a low-acid crude of similar bulk character, an upgraded or synthetic crude, or a stream that has been chemically treated. Second, the model cannot track a change in acidity within a single crude, because within a single crude the bulk descriptors that carry the correlation are nearly constant — which is precisely the process-control use case for which such a model is most often proposed. Third, validation designs that draw calibration and test sets randomly from the same population of natural crudes will overstate performance, because the geochemical covariance is present in both sets; validation must include samples in which acid number has been varied deliberately at constant bulk composition, by spiking or by controlled partial deacidification, if the model is to be trusted outside its calibration family.

The remedy is not to abandon multivariate calibration but to anchor it. Where a chemometric acid number model is deployed, the reference values used to build and to audit it should be obtained by a method that measures carboxyl content specifically — the phosphitylation route of Section 8.3, or the esterification route of Section 8.2, or the infrared naphthenic acid number [27] — rather than by titration alone, and the calibration set should include a designed spiking series that breaks the collinearity between acidity and crude family. A model validated in this way can be defended; a model validated only against titration on a convenience sample of natural crudes cannot.

9.3 A Measurement Map for the Recovery and Purification Train

Where NMR earns its place unequivocally is downstream of the crude, in the naphthenic acid recovery and refining plant itself, because the acid concentration rises by two to three orders of magnitude across the caustic extraction step and every sensitivity objection raised in Section 8.1 disappears. Table 6 maps the process stages described in Section 5 onto the NMR measurement appropriate to each. Entries describing established measurement principles are distinguished in the text from those proposed here for development.

Table 6. Proposed NMR measurement map for a naphthenic acid recovery and purification train. Measurement principles marked ‘established’ rest on published, validated practice; those marked ‘proposed’ are put forward in this paper as technically sound applications of established principles to a stage where, to the author's knowledge, they have not been formally validated.

Process stage	Control question	NMR measurement	Status
Distillate feed to caustic wash	How much extractable acid is entering, and of what type?	Benchtop ^{1}H NMR with multivariate calibration for screening; ^{31}P phosphitylation for a specific carboxyl determination	Established / proposed
Caustic extraction stages	What fraction of the acid has transferred, and is the carboxylate fully ionized?	^{1}H NMR of the aqueous phase with solvent suppression; the α-CH_2 resonance shifts upfield by roughly 0.2 ppm on deprotonation, giving a direct spectroscopic measure of the degree of neutralization	Proposed
Treated distillate	Has the acidity specification been met?	Benchtop ^{1}H NMR after methyl esterification, integrating the OCH_3 singlet against an internal standard	Proposed
Springing	Is acidulation complete and is soap carryover controlled?	^{1}H NMR of the separated organic phase: reappearance of the acid-form α-CH_2 shift and loss of the carboxylate shift	Proposed
Dehydration	How much water remains?	^{31}P determination of water through the	Established

Process stage	Control question	NMR measurement	Status
		hydroxylated-reagent resonance, concurrent with acid value; or time-domain relaxometry for bulk water	
Neutral oil removal	How much unsaponifiable hydrocarbon remains?	Ratio of the acid-associated proton population to total aliphatic proton integral after esterification, calibrated against gravimetric unsaponifiables	Proposed
Vacuum fractionation	What is the average molecular weight and ring content of each cut?	Combined ^{1}H and ^{13}C average molecular parameter analysis on grab samples	Established
Product release	Acid value, water, phenolic content in one measurement	^{31}P phosphitylation with certified internal standard	Established in principle, requires validation for this matrix
Metal naphthenate manufacture (Zn, Zr, Ca)	Has conversion of free acid to carboxylate gone to completion?	^{1}H and ^{13}C carbonyl shift on salt formation; residual free acid by esterification qNMR	Proposed
Metal naphthenate manufacture (Co, Mn, Fe)	What is the metal loading?	Paramagnetic relaxation enhancement: ^{1}H T_1 and T_2 of the solution scale with paramagnetic metal concentration, giving a rapid at-line assay by time-domain NMR	Proposed

Two entries in Table 6 deserve expansion because they are the least obvious and, in the author's judgment, the most promising. The first is the caustic-extraction measurement. Deprotonation of a carboxylic acid shifts the resonance of the protons on the alpha carbon upfield by approximately 0.2 ppm, because the electron-withdrawing character of the carboxyl group is reduced on conversion to carboxylate. In an aqueous naphthenate solution this shift is directly observable by proton NMR with solvent suppression, and the ratio of the acid-form and salt-form alpha resonances reports the degree of neutralization without titration and without phase separation. The measurement is straightforward in principle; what requires development is the handling of a highly alkaline, strongly ionic, hydrocarbon-contaminated aqueous stream in a flow cell.

The second is the paramagnetic assay of cobalt and manganese naphthenate driers. Cobalt(II) and manganese(II) are strongly paramagnetic and shorten the longitudinal and transverse relaxation times of the surrounding solvent protons in proportion to their concentration, which is the same relaxivity relationship that underpins contrast agent behavior in magnetic resonance imaging. A time-domain relaxometer measuring T_1 or T_2 on a drier solution would therefore return metal content in seconds, non-destructively, on the neat product, in a matrix where conventional metal assay requires digestion or X-ray fluorescence. The relationship must be established empirically for each metal and each solvent system, and it will be sensitive to speciation and to the presence of other paramagnetic species, but as a rapid at-line consistency check on a manufactured drier it is an attractive proposition. It is offered here as a hypothesis worth testing, not as a validated method.

9.4 Relaxometry and Diffusion for Emulsion and Deposition Problems

The upstream problems of Sections 4.3 and 4.4 are addressed by a different family of NMR measurements. Water content and droplet size distribution in a water-in-crude emulsion are determined by relaxation and

pulsed field gradient diffusion methods on the intact, opaque sample [45,46], and diffusion-ordered spectroscopy resolves the molecular size distribution of the acids responsible for stabilizing that emulsion [44]. Where a naphthenate soap emulsion is suspected, the combination of a droplet size distribution, a water content, and a proton spectrum showing carboxylate rather than carboxylic acid alpha-proton shifts constitutes a coherent diagnostic package that can be assembled in under an hour on benchtop and time-domain hardware. Relaxation-based crude oil characterization more generally, including its coupling to machine learning approaches for viscosity and density prediction, has been reviewed recently [40].

9.5 Practical Constraints on Plant Deployment

Several constraints recur in every attempt to place NMR on a petroleum process stream and they should be designed for at the outset rather than discovered during commissioning. Sample temperature must be controlled and elevated relative to ambient, both because viscosity broadens resonances through restricted molecular tumbling and because wax crystallization below the cloud point removes the crystalline fraction from the observable liquid signal entirely, biasing every integral in the spectrum. Entrained water produces a resonance that shifts with temperature and ionic content and, more damagingly, produces magnetic susceptibility discontinuities that broaden the entire spectrum; a coalescer or a phase separator ahead of the analyzer cell is generally necessary. Paramagnetic species indigenous to crude — vanadyl and nickel porphyrins and the free radical population associated with asphaltenes — shorten relaxation times and broaden lines in the heaviest streams. Solids and scale foul flow cells and shift the sample from the region of magnetic homogeneity. Finally, and most often underestimated, the reference laboratory method against which the analyzer is calibrated carries its own reproducibility, and an analyzer cannot be validated to a precision better than that of the reference data used to build it; where the reference is a titrimetric acid number on a dark viscous crude, that reproducibility is not small.

10. Orthogonal and Complementary Techniques

No single technique characterizes naphthenic acids adequately, and the selection of a method should follow from the question rather than from instrument availability. Titration returns a neutralization number rapidly and cheaply but is unselective [25,26]. Infrared spectroscopy responds specifically to the carboxyl carbonyl and provides both a naphthenic acid number determination and, in chemometric form, a total acid number prediction, at the cost of sensitivity to the monomer–dimer equilibrium and to matrix absorption [27,28]. Gas chromatography, in its high-temperature and comprehensive two-dimensional forms and generally following derivatization, resolves individual congeners within the volatile fraction and remains the route to the ARN tetraacids [12,14]. Negative-ion electrospray FT-ICR and Orbitrap mass spectrometry resolve elemental composition across thousands of species and constitute the reference technique for compositional description [5,6,7]. NMR spectroscopy returns bulk-average structure, aromaticity, and — through derivatization — absolute functional group quantification without response factors. Table 7 sets these against one another on the criteria that determine method selection in practice.

Table 7. Comparison of the principal analytical approaches to naphthenic acid characterization.

Criterion	Titration	FTIR	GC and GC×GC	FT-ICR MS	NMR
Selective for carboxyl	No	Yes	Yes, after derivatization	Yes	Yes, after derivatization
Congener resolution	None	None	High within	Very high	None

Criterion	Titration	FTIR	GC and GC×GC	FT-ICR MS	NMR
			volatile range		
Distinguishes ring from aromatic unsaturation	No	Partially	By retention behavior only	No	Yes, directly
Quantitative without response factors	Yes	No, requires calibration	No	No	Yes
Sensitivity in whole crude	Adequate	Adequate	High after extraction	Very high	Poor without derivatization
Non-volatile and high-mass species	Included	Included	Excluded above the volatility limit	Included	Included
Speed and suitability for process use	Minutes, off-line	Seconds, on-line capable	Tens of minutes, off-line	Off-line, specialist	Seconds to minutes, on-line capable
Capital and operating cost	Low	Low	Moderate	Very high	Moderate (benchtop) to high (high-field)

The practical conclusion is that a defensible characterization of a naphthenic acid stream requires at minimum a neutralization number, a carboxyl-specific determination, and a compositional description, and that these are three different measurements. The pairing of NMR with high-resolution mass spectrometry is the most information-dense combination available, and published petroleum acid studies increasingly adopt it [41,42].

11. Critical Assessment: Where NMR Fails and Where Claims Are Vulnerable

A white paper that recommends a technique without stating its failure modes is of limited use to the person who has to defend a result. This section states them plainly, and is written from the perspective of the reviewer, auditor, or opposing technical expert who will examine the work.

11.1 What NMR Cannot Do

NMR cannot resolve individual naphthenic acid congeners, cannot determine a carbon number distribution, and cannot determine a Z-family distribution. Any claim to the contrary should be treated as an error. NMR cannot detect the C_{80} tetraacids in whole crude at the parts-per-million concentrations at which they cause deposition; their determination requires selective isolation followed by chromatography or mass spectrometry, with NMR entering only at the structure-confirmation stage on isolated material [12,13,14,11]. NMR cannot, without derivatization or extraction, determine carboxyl content in whole crude oil at industrially relevant acid numbers, for the arithmetic reasons set out in Section 8.1. NMR provides no useful observable for color, and none for sulfur content at typical concentrations.

11.2 Specific Technical Vulnerabilities

Where NMR-based naphthenic acid results are challenged, the challenge will normally fall on one of the following points. Quantitative carbon spectra acquired without inverse-gated decoupling and without a relaxation agent will under-report the non-protonated carboxyl carbon, and the magnitude of the error is not small. Recycle delays set by habit rather than by measured relaxation times produce the same defect in

proton experiments where an exchangeable or slowly relaxing resonance is involved. Derivatization completeness asserted rather than demonstrated is a standing vulnerability of every method in Section 8, and the appropriate defense is a spike-recovery experiment on the actual matrix. Baseline and phase correction applied aggressively will erode a broad minor resonance sitting on a curved background, and the resulting bias is invisible in the reported integral. Samples measured below the cloud point will have lost the crystallized wax fraction from the observable signal, biasing every normalized integral in the spectrum. Aqueous naphthenate samples measured without adequate solvent suppression, or with suppression that also attenuates nearby analyte resonances through radiation damping or presaturation transfer, will be quantitatively wrong in a manner that is not apparent from the spectrum.

A distinct and more consequential vulnerability attaches to chemometric results. As set out in Section 9.2, a partial least squares prediction of total acid number from a low-field proton spectrum does not observe the acid, and a report that describes such a result as an NMR determination of acid number invites a challenge that is difficult to answer. The defensible formulation states that the acid number was predicted from a multivariate model calibrated on a stated population, reports the calibration range and the external validation statistics, and states the conditions under which the model is not applicable. Reporting a prediction outside the calibration domain, or reporting it without the domain, is the specific failure that an opposing expert will pursue, and rightly.

11.3 A Caution on the Acidity–Corrosivity Inference

One further inferential trap deserves emphasis because it lies outside NMR practice but is frequently reached through it. Total acid number is widely used as a corrosivity index and blending constraint, and it is a poor one. Corrosion rate in the crude unit depends on the acid population, on the sulfur species present, on temperature, on wall shear stress, and on the stability of the sulfide and oxide scales formed under the prevailing conditions, and the mechanistic evidence indicates that these interact rather than superpose [21,19,20]. A rapid, accurate, spectroscopically anchored acid number improves the input to a corrosivity assessment; it does not make the assessment correct. Any recommendation deriving from an acid number should be framed accordingly, and a claim that a crude is non-corrosive because its acid number is low is not supportable on that evidence alone.

12. Recommended Analytical Workflows

12.1 Refinery Acidity Screening on Incoming Crude

For rapid screening of receipts and blend components, benchtop proton NMR with a multivariate acid number model provides a result in minutes on a neat sample and is well suited to the purpose, provided the constraints of Section 9.2 are respected. The recommended configuration pairs the chemometric screen with a periodic anchor: a phosphitylation determination on a subset of samples, at a frequency sufficient to detect model drift, and mandatory anchoring whenever a new crude family enters the slate. Samples flagged near a metallurgical or contractual threshold should be confirmed by the reference titration and by a carboxyl-specific determination rather than released on the model prediction alone.

12.2 Quality Control of Recovered Naphthenic Acid Products

For a recovered acid product the recommended primary measurement is phosphorus-31 NMR following phosphitylation, which returns acid value, phenolic acid content, aliphatic hydroxyl content, and water content from a single acquisition against a certified internal standard. This is supplemented by a quantitative

proton spectrum for average structural parameters and aromaticity, by esterification quantitative NMR as an independent check on acid value, and by the conventional determinations for color and sulfur, for which NMR offers nothing. The value of the phosphorus experiment in this application is that it replaces three separate wet-chemical determinations, one of which — phenolic acid content — is otherwise laborious.

12.3 Deposit and Soap Emulsion Forensics

Where a production facility presents a separation upset, the diagnostic objective is to distinguish calcium naphthenate deposition from sodium naphthenate soap emulsion, since the treatments differ. The recommended sequence begins with time-domain relaxometry and pulsed field gradient diffusion on the intact emulsion to establish water content and droplet size distribution [45,46], proceeds to proton NMR of the separated aqueous and organic phases to establish whether the acids present are in acid or carboxylate form, and, where solid deposit is available, proceeds to extraction of the deposit and determination of C_{80} tetraacid content by the established chromatographic route [13,14] with high-field NMR confirmation of structure on isolated material where the identification is contested [10,11]. Diffusion-ordered spectroscopy on the isolated acid fraction distinguishes the molecular size population and, by comparison with a commercial naphthenic acid reference, indicates whether the indigenous acids are of unusually high molecular weight [44].

12.4 Deacidification Process Development

For development or optimization of an esterification, decarboxylation, extraction, or adsorption deacidification process [59,60,58,42], NMR is unusually well suited because it observes reactants and products simultaneously and without separation. In an esterification study the disappearance of the alpha-proton resonance of the free acid and the appearance of the ester methoxyl singlet are followed in the same spectrum, and conversion is obtained directly from their ratio with no calibration required. In a decarboxylation study the carbonyl region of the carbon spectrum distinguishes residual acid from the ketone products formed [22], which a titration cannot. In an extraction study the aqueous and organic phases can each be examined and the mass balance closed. Reaction monitoring in continuous-flow configuration on benchtop hardware is established practice and the relevant acquisition parameter trade-offs have been characterized [57]. The recommended configuration for a bench-scale continuous unit is a benchtop spectrometer on a recirculating slipstream, with periodic grab samples sent for phosphitylation determination to anchor the on-line result.

13. Conclusions

Naphthenic acids are best understood not as a compound class but as an operationally defined fraction whose internal heterogeneity is the source of both its industrial impact and its analytical difficulty. The classical $C_nH_{2n+z}O_2$ formalism, though useful, conflates saturated rings with aromatic rings and olefinic unsaturation and should not be relied upon for structural inference without independent measurement of aromaticity. The tetraprotic ARN acids are a distinct subclass whose deposition behavior is disproportionate to their concentration and which require dedicated analytical treatment.

For NMR spectroscopy the central conclusion is a matter of arithmetic. At industrially relevant crude acid numbers the carboxyl functionality represents of the order of one part in ten thousand of the observable nuclear inventory, and direct determination in whole crude is therefore not achievable; in a recovered acid concentrate the same functionality represents several percent, and determination is straightforward. Between these two regimes lie the two strategies that make whole-crude NMR determination possible: chemical amplification by derivatization into a background-free nucleus, of which phosphorus-31

phosphitylation is the most powerful available and the author's recommended reference approach, and multivariate calibration, which is operationally valuable but is a correlation with bulk composition rather than a measurement of acid and must be reported and bounded as such.

Where NMR is uniquely strong is in the properties that mass spectrometry cannot supply: direct measurement of aromaticity, branching, ring-junction methine content, and average molecular structure, all without response factors; simultaneous speciation of carboxylic, phenolic, alcoholic, and aqueous protic functionality in a single phosphorus experiment; carbonyl speciation that distinguishes acid from ester from ketone in thermally stressed streams; and relaxation and diffusion observables that characterize the emulsions and interfacial films through which these acids exert much of their operational damage. Deployed on the recovery and purification train, where concentration is high and the analytical questions are quantitative and repetitive, benchtop and time-domain NMR are capable of replacing several separate wet-chemical determinations with a single rapid measurement. That, rather than the displacement of mass spectrometry, is where the practical value of NMR in naphthenic acid chemistry is to be found.

Several of the applications proposed in Sections 8 and 9 — the spectroscopic acid value and its comparison with the titrimetric total acid number, the carboxylate shift as a measure of neutralization in caustic extraction, the spectroscopic estimation of unsaponifiable neutral oil, and paramagnetic relaxation assay of cobalt and manganese drier products — are put forward as methodologically sound proposals rather than as validated procedures. Each rests on established physical principles and each would require method development, spike-recovery validation, and uncertainty characterization before deployment in a laboratory operating under ISO/IEC 17025. They are identified as such here so that they are not mistaken for accepted practice.

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All entries were verified through the CrossRef REST API before drafting; title, complete author list, journal, year, volume, issue, and pagination were confirmed against the CrossRef record in each case. Reference numbers are set at full size in this list; in-text citations are set as superscripts.

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Summary

Naphthenic acids are the collective carboxylic acid content of crude petroleum, an operationally rather than chemically defined fraction comprising acyclic branched acids, mono- through polycyclic alicyclic acids, aromatic and heteroatomic acids, polyoxygenated species, and the C_{80} to C_{82} isoprenoid tetraprotic ARN acids. They arise principally from in-reservoir biodegradation, which explains their association with heavy, low-gravity crudes and their concentration in the heavier distillation cuts. Within the refinery they drive high-temperature corrosion in the 200 to 400 °C window through formation of oil-soluble iron carboxylates, a mechanism that interacts with sulfidation rather than superposing on it and that consequently correlates poorly with total acid number alone. In production they form metal naphthenate deposits and soap emulsions and stabilize water-in-crude emulsions that resist desalting. Recovered from refinery spent caustic by springing, dehydration, neutral oil removal, and vacuum fractionation, they support a commercial trade in metal carboxylates used as coating and ink driers, cure catalysts, tire-cord adhesion promoters, wood preservatives, lubricant and fuel additives, and corrosion inhibitor intermediates.

The measurement conventionally used to control all of this, the titrimetric total acid number, is a bulk neutralization number that responds to phenols, sulfur species, and inorganic acidity as well as to carboxylic acids, and it therefore does not measure the compound class it is used to represent. The analytical opportunity for NMR lies in that gap, but the opportunity is bounded by sensitivity in a way that should be understood quantitatively rather than qualitatively. At a total acid number of 0.5 mg KOH per gram, the carboxyl proton constitutes approximately seventy parts per million of the total proton integral of a crude oil, and the carboxyl carbon approximately one hundred and twenty-six parts per million of the carbon integral; direct observation is arithmetically excluded. In a recovered acid product of acid value 230 mg KOH per gram, the same proton constitutes roughly four percent of the integral and the methoxyl group of its methyl ester roughly ten percent; direct observation is routine.

Three quantification strategies follow from this. Esterification places three sharp methoxyl protons per carboxyl in a spectral window that is vacant in petroleum, permitting a standard-referenced spectroscopic acid value whose difference from the titrimetric total acid number measures the non-carboxylic acidity of the sample. Phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane transfers the determination to phosphorus-31, a nucleus with no hydrocarbon background at all, and resolves carboxylic acid, phenolic acid, aliphatic hydroxyl, and water in a single spectrum; this is the recommended reference approach, subject to control of solubility, water content, thiol interference, and derivative stability. Fluorine-19 derivatization is recommended as a complement for carbonyl speciation in thermally stressed streams rather than as a primary acid determination. Alongside these, multivariate calibration of low-field proton spectra against acid number is operationally valuable and well documented, but it correlates acidity with bulk hydrogen distribution rather than observing the acid, and it will fail wherever acidity has been decoupled from bulk composition — which includes the single-crude process-control case for which it is most often proposed. Such models should be anchored to a carboxyl-specific reference method and validated against a designed series in which acid number varies at constant bulk composition.

The strongest practical case for NMR is on the naphthenic acid recovery and purification train, where the acid concentration is two to three orders of magnitude higher than in the crude and where a single phosphorus experiment can replace separate determinations of acid value, phenolic content, and water. NMR is also uniquely able to resolve the ring-versus-aromatic ambiguity inherent in mass-spectrometric hydrogen deficiency values, to speciate acid, ester, and ketone carbonyls in stressed streams, and to characterize emulsion water content, droplet size, and acid molecular size distribution on intact opaque samples. NMR cannot resolve congeners, cannot determine carbon-number or Z-family distributions, and

cannot detect the ARN tetraacids at their operative concentrations without prior isolation; on those questions high-resolution mass spectrometry and chromatography remain the necessary techniques. The two families of method are complementary, and a defensible characterization of a naphthenic acid stream requires a neutralization number, a carboxyl-specific determination, and a compositional description — three distinct measurements that no single instrument supplies.

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