Received: 14 August 2023 | Accepted: 19 February 2024

DOI: 10.1002/jpln.202300268

REVIEW

Potential pitfalls when using popular chemical extractions to characterize Al- and Fe-containing soil constituents

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This article has been edited by Karin Eusterhues.

Abstract

Wet-chemical extraction of soil to quantify pedogenic species or to remove specific compounds prior to other analyses is an established approach in analytical soil mineralogy and soil chemistry. Interpretation and informational value of data derived from long-established and frequently used extractions, for instance involving dithionite, oxalate/oxalic acid in the dark (AOD), and pyrophosphate (PYR), suffers from nonuniform practical regulation and missing knowledge about potential methodical limitations. In this review, we analyzed potential pitfalls of these frequently used extractions, with the focus on selectivity and completeness of the methods as derived from effects of time dependency and of phase separation. Major problems we identified comprised that time-dependency of extraction differed between analytical targets, that a multitude of species is attacked, reducing the selectivity for the original analytical target, and that studies on extraction from model compounds, including analytical targets and nontargets, are not universally present. The latter aspect is crucial for the completeness of AOD and PYR extraction that has not been proven for all potential analytical targets of the methods yet. We practically tested citrate (CIT) extraction of aluminum (Al) and iron (Fe) in organic association, using selected models of soil constituents. Apart from a synthesized poorly ordered Si-rich short-range ordered aluminosilicate, CIT did not extract Al from nontarget phases, confirming previous studies, but did extract Al and Fe completely from organic associations. In addition to recommendations on the practical use of dithionite-based, AOD, citrate-ascorbate (CA), and CIT extraction, we suggest replacing highly problematic PYR extraction by CIT extraction for metals in organic association in soil and using AOD extraction in combination with CA and CIT extraction to avoid potential misinterpretation of ambiguous data.

KEYWORDS
aluminum, dithionite, iron oxides, organic association, oxalate, secondary minerals

1 | INTRODUCTION

Application of chemical extractions has a long tradition in analytical soil mineralogy and soil chemistry, as evident from several reviews (e.g., Borggaard, 1988; Parfitt & Childs, 1988; Rennert, 2019; Voelz et al., 2019). Chemical extractions are based upon transferring elements, here aluminum (Al) and iron (Fe), from soil into the aqueous phase for further analysis. These elements belong to the most abundant ones in soil, and the reasons for their chemical removal from the soil matrix may be either preparation of soil samples for subsequent analyses or characterization of soil and separates of soil. An example for the former motivation is the use of dithionite-based extraction methods to remove Fe oxides (the term "Fe oxides" comprises the entirety of Fe oxides, hydroxides, and oxyhydroxides in this paper) from clay minerals and from soil prior to X-ray diffractometry by dissolution (Galabutskaya & Govorova, 1934). Extraction with acidic oxalate solution (Tamm, 1922) is an example of the latter and is used to dissolve Al and Fe in X-ray amorphous forms from soil.

The original dithionite method was modified by introducing citrate as complexing agent (Aguilera & Jackson, 1953) and bicarbonate as buffer (Mehra & Jackson, 1958), consequently abbreviated as "DCB" method. Tamm (1922) extracted soil with oxalate/oxalic acid in the presence of light, but Schofield (1950) realized that more crystalline Fe oxides are attacked in addition to the actual target of extraction, which is restricted to X-ray amorphous Al and Fe species. Schwertmann (1964) showed that the type of light (diffuse daylight, sunlight, and UV light) determines the extent of dissolution of nontarget phases and inferred the exclusion of light during extraction with oxalate/oxalic acid. Thus, the method is frequently designated as "AOD" method (ammonium oxalate-oxalic acid in darkness). The DCB method by Mehra and Jackson (1958) has become very common for the quantification of ferric Fe in Fe oxides, and the AOD method by Schwertmann (1964) for quantification of Al and Fe in X-ray amorphous forms in soil, including X-ray amorphous, poorly crystalline Al- and Fe-containing minerals, as evident from a four-digit number of total citations of both papers. The conditions of Schwertmann's AOD method (pH 3, 0.2 M ammonium oxalate, and 0.2 M oxalic acid) were adapted by McKeague and Day (1966), which is a similarly often cited paper, and used for soil classification, for instance, according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2022) and the US Soil Taxonomy (Soil Survey Staff, 2022a).

Similarly widespread is the use of pyrophosphate (PYR) for Al and Fe in organic forms, originally reported by Bremner et al. (1946). Their method was modified by Bascomb (1968) and McKeague (1967) by raising the pH to 10, which is now frequently used. The two-step approach developed by Reyes and Torrent (1997), using citrate-ascorbate (CA) and citrate (CIT), combines some of the analytical targets of AOD and PYR extraction, Al and Fe ions complexed by soil organic matter (SOM), and poorly crystalline Fe oxides. Remarkably, ascorbate does not mobilize X-ray amorphous, inorganic Al phases, as ascorbate is a reductant. Consequently, the combined application of AOD and CA + CIT extractions may give a more detailed approximation of Al and Fe in certain forms than AOD alone. For instance, AOD dissolves Al in organic association, associated with AOD-soluble Fe oxides (either adsorbed or structurally incorporated) and short-range-ordered aluminosilicates (SROAS), but to unknown proportions (summarized by Rennert, 2019).

The widespread use and the informational value of the popular chemical extractions for Al and Fe are beyond question. Nonetheless, there are several problems, open questions, and practical pitfalls associated with the chemical extractions mentioned before. The aim of this paper was to identify potential pitfalls of the methods and to offer solutions how to deal with them, rather than to review the principles of extraction and to summarize their use in soil science, as several reviews already exist (e.g., Borggaard, 1988; Parfitt & Childs, 1988; Rennert, 2019; Voelz et al., 2019). A further aim of this study was to test the completeness of Al and Fe extraction from models of metal–organic associations by CIT at pH 6 (Reyes & Torrent, 1997). This extractant does not mobilize Al and Fe from nontarget minerals, including Fe oxides and a variety of primary and secondary silicates (Rennert et al., 2021). However, the completeness of Al and Fe extraction from the analytical target, metals in organic association, has not been checked yet.

2 | PROBLEMS AND POTENTIAL PITFALLS WITH CHEMICAL EXTRACTIONS TO CHARACTERIZE Al AND Fe IN SOIL

2.1 | Selectivity and completeness

Apart from completeness of extraction, that is, the entirety of the analytical target forms is permanently dissolved, selectivity of extraction is desired, and that is, only the targets are dissolved and can thus be quantified. Concomitantly, any release of the target element from nontarget phases should not occur at best. Actually, ferrihydrite, lepidocrocite, akaganeite, and often goethite are completely dissolved by DCB extraction (Rennert, 2019; Voelz et al., 2019). However, dissolution of magnetite by DCB is not complete, and that of hematite, goethite, and maghemite may be incomplete. Consequently, the completeness of DCB extraction regarding targeted ferric Fe in oxides depends on the composition of the soil sample. Holmgren (1967) developed a dithionite-based extraction method, which is frequently used and has become part of the laboratory methods used for Soil Taxonomy in similar form (Soil Survey Staff, 2022b). The Holmgren (1967) method differs from that by Mehra and Jackson (1958) in the lower temperature during extraction (20 vs. 80°C), the singular addition of dithionite (a singular addition vs. one or two repeated additions of dithionite), the lack of bicarbonate as buffer, and the longer duration of extraction ("overnight" vs. 15 min). Thurman and Ciolkosz (1992) compared both methods with soil samples, and the amounts of Fe extracted after Mehra and Jackson (1958) exceeded those extracted after Holmgren (1967), but the difference was not significant. However, the amounts of Al extracted by the former method exceeded those of the latter significantly. Similarly, Inda Junior and Kämpf (2003) detected that more Fe was extracted using the Mehra and Jackson

(1958) method than using the Holmgren (1967) method from soil dominated by goethite, depending on the degree of Al substitution of goethite, whereas there was no difference between the methods with hematite-dominated soil. Sheldrick and McKeague (1975) did not detect varying extent of Al and Fe extraction, applying the Mehra and Jackson (1958) method versus extraction at room temperature and overnight. The partially lower yield of the Holmgren (1967) method may be caused by the rapid loss of the reduction capacity of dithionite after 15 min (Pansu & Gautheyrou, 2003), which is circumvented by the repeated addition of dithionite with the Mehra and Jackson (1958) method.

Additionally, DC(B) may induce the release of Al, Fe, and Si from nontarget sources, including various silicates and metal–SOM associations, as summarized by Rennert (2019), so that sensitivity may be limited. Dissolved Al in DC(B) extracts may be interpreted as Al in metal–SOM complexes, Al previously incorporated into Fe oxides or adsorbed on their surfaces, but the proportion of Al released from nontarget phases in DC(B) extracts is not predictable. In any case, Al in DC(B) extracts must not be interpreted as Al from Al oxides/hydroxides, irrespective of their crystallinity, which would be a wrong analogy to ferric oxides, as dithionite does not reduce Al(III). The very likely release of Al and Fe from organic associations to unknown and varying extent is caused by neutral to alkaline extraction pH and the use of CIT as complexing agent in both the Mehra and Jackson (1958) (0.3 M Na-citrate at pH 7.3) and the Holmgren (1967) method (0.75 M Na-citrate at variable pH, from slightly acidic to alkaline, depending on soil), similar to the CIT extraction, using 0.2 M Na-citrate CIT at pH 6.

A comprehensive statement on selectivity and completeness of the AOD method is even more difficult, if not impossible. Schwertmann (1959, 1964) exclusively targeted Fe in X-ray amorphous oxide forms and aimed to develop a wet-chemical method for a qualitative characterization of Fe oxides in soil, suggesting the quotient of the contents of AOD- and DCB-extractable Fe. McKeague and Day (1966) extended the analytical focus of AOD extraction by including Al in the quantitative analysis of the extract, by the combination of AOD and DCB extraction, and by X-ray diffractometry of the samples before and after extraction. Based on the similar release of Al and Fe at pH 2 and 3 from soil under study, these authors concluded that dissolution driven by acidic pH was not the main process inducing the release of Al from soil into the aqueous phase by AOD, but metal complexation. This result pointed to an additional organic source of AOD-extractable Al and Fe in soil, as already suggested by Schwertmann (1964) for Fe and by McKeague and Day (1966) for Al. These organic forms are X-ray amorphous as well. Actually, a large fraction of the AOD-extractable Al (up to 87%) and Fe (up to 86%) in subsoil horizons (Bg, Bl, and Bw) of Cambisols, Gleysols, and Stagnosols was in organic association, as extracted by CIT at pH 6 (Rennert et al., 2021). Thus, the organic contribution to AOD-extractable Al and Fe may even exceed the oxidic contribution, so that the suggested quotient of the contents of AOD-extractable and DCB-extractable Fe as an indicator of the crystallinity of Fe oxides may be valid to an unknown extent only. Consequently, an additional and reliable quantification of Al and Fe in organic forms is required to correct the AOD-extracted contents, when used to indicate the degree of crystallinity of Fe oxides. The same applies to the approximation of the ferrihydrite contents in soil by multiplying the content of AOD-extractable Fe by a constant factor (e.g., Childs, 1985), which is not universally valid, but depending on the organic contribution to AOD-extractable Fe. However, the variety of different secondary Fe phases formed in soil makes it very difficult to establish a border between poorly crystalline Fe oxides and Fe in organic association, and thus between the analytical targets. Coprecipitation of Fe with dissolved organic matter (DOM) effectively removes DOM from the aqueous phase (e.g., Eusterhues et al., 2011), but apart from amorphous flocs (Henneberry et al., 2012), crystallites of poorly crystalline Fe oxides such as ferrihydrite and lepidocrocite associated with OM form (e.g., Chen et al., 2016; ThomasArrigo et al., 2018). Consequently, subtraction operations such as $Fe_{AOD} - Fe_{PYR}$ for Fe in poorly crystalline Fe oxides or $Fe_{DCB} - Fe_{AOD}$ for Fe in crystalline Fe oxides are questionable because of the incomplete selectivity of the extractants and the resulting nonadditive fractions extracted (cf. Vodyanitskii & Shoba, 2014). Similarly, Bertsch and Bloom (1996) emphasized the operational nature of these extractants used for Al, which are consequently not selective for specific phases.

Approaches to quantify SROAS using AOD extraction suffer from deficient selectivity regarding even two elements, Al and silicon (Si). As mentioned before, AOD extracts Al in organic forms as well, which was aimed to be corrected by subtracting PYR-extractable Al for allophane quantification (Mizota & van Reeuwijk, 1989; Parfitt, 1990). However, the selectivity and extent of PYR extraction in general strongly depends on phase separation (Section 2.4), limiting this approach. Additionally, the completeness of AOD extraction of Al and Si depends on both extraction time and phase separation, that is, the separation of the liquid phase (extract) from the extracted solid phase, usually soil (Sections 2.3 and 2.4). Finally, AOD extraction of Al and Si is not selective, as AOD extracts, apart from organic sources mentioned before, Al from AOD-soluble Fe oxides, from poorly crystalline Al oxides, and hydroxy-interlayer Al (summarized by Rennert, 2019). Rennert et al. (2014) showed a systematic overestimation of Si in SROAS by AOD extraction, derived from a comparison with ^{29}Si-NMR data, as, similar to Al and Fe, Si in AOD extracts derives, apart from SRAOS, from several sources, including adsorbed silica or Si incorporated in Fe oxides (Rennert et al., 2021).

Summarized, the problems regarding a comprehensive statement on selectivity and completeness of the AOD method are that (1) the original analytical target (X-ray amorphous Fe oxides and other Al- or Fe-containing species) is chemically very heterogeneous among different pedogenetic environments, (2) the chemical nature of particularly Al–SOM associations is poorly understood, and (3) a comprehensive study on the selectivity and completeness of AOD extraction using models of the analytical targets and extracted nontargets is lacking. Some studies on the extraction of defined target and nontarget Al and Fe (and Si) species by AOD actually exist (e.g., Rennert & Lenhardt, 2022; Rennert et al., 2021; Reyes & Torrent, 1997), but these were limited to minerals (primary and secondary silicates, Fe oxides, and Al oxides), excluding organic forms. However, this is not astonishing,

considering aspect (2)—the nature of organic AOD-extractable forms of Al and Fe remains ambiguous.

The use of PYR to extract Al and Fe from organic associations has been criticized several times in the past because of the mobilization of nontarget particles by dispersion (Section 2.4) and the release of Al from poorly crystalline Al hydroxides (up to 80% of Al; McKeague et al., 1971), Al-hydroxy interlayers, and to small extent from gibbsite and SROAS (summarized by Rennert, 2019). Additionally, extraction at pH 10 generally induces partial release of Al from clay minerals (Carroll & Starkey, 1971). Consequently, Paterson et al. (1993) considered the Al fraction extracted from soil by PYR at pH 10 ill-defined. A problem with Fe arises, as complexes between Fe and extracted fulvic acids (which might be considered a model of natural SOM), are stable up to pH 9, while at pH 10 hydrous Fe oxides form (Schnitzer & Skinner, 1963). Consequently, the analytical target may react and change during PYR extraction at pH 10. PYR extraction did not release Fe from "amorphous Fe silicate", "amorphous Fe oxide", goethite, and hematite (McKeague, 1967). However, based on X-ray absorption spectroscopy, Karlsson et al. (2008) concluded that PYR does not preferentially extract Fe from organic complexes in organic soils, and their results were contrary to the assumed extraction specificity. Although the selectivity of PYR at least for organic Al can be negated at pH 10, even at optimal conditions of phase separation (Section 2.4), completeness of PYR extraction using defined model substances has not been comprehensively studied, similar to that of AOD extraction. The studies on completeness were restricted to humic substances extracted from soil by NaOH (e.g., McKeague et al., 1971; Takahashi et al., 2007) or by a mixture of acetyl acetone and even PYR (Higashi, 1983), and complexes with Al and Fe were then produced by adsorption experiments. A single extraction of the complexes with adsorbed metal cations was partially complete but also incomplete to large extent in these studies, depending on the metal and the humic substance used. Furthermore, Wada and Higashi (1976) showed that the extent of Al and Fe extraction increased with repetition of PYR extraction (up >50% after the fifth repetition). Additionally, it is questionable whether PYR attacks the entirety of SOM, as it dissolves preferentially SOM rich in carboxyl groups rather than SOM rich in phenolic groups (Hayes & Swift, 2018), both of which form complexes with metals. As far as we know, there is no comprehensive study that verified the completeness of PYR extraction of Al and Fe in organic association using several realistic models of the potential organic forms of the metals, including the analytical boundary conditions of extraction such as time and number of necessary repetitions.

Rennert et al. (2021) and Reyes and Torrent (1997) have studied the selectivity of individual CA and CIT extraction regarding Al- and Fe-containing minerals. However, comprehensive information on selectivity and completeness of the extraction of Al and Fe by CIT from defined metal–organic associations is lacking, apart from the study by Gerke (1993), who studied the Fe release by CIT from a "poorly ordered Fe oxide" and Fe complexes with humic substances. Therefore, we tested the completeness of CIT extraction of Al and Fe from selected models of metal–organic associations and selectivity using further analytical nontargets, as described in the following section.

2.2 | Extraction of Al and Fe from models of metal–organic associations by CIT

2.2.1 | Materials and methods

We tested the extraction of Al and Fe by CIT at pH 6 (Reyes & Torrent, 1997) from models of pedogenic species. These compounds comprised two SROAS with different Al:Si ratios, two coprecipitates formed by the reaction of Al, Si, and DOM, flocs formed by precipitation of Al or Fe ions with DOM, and charred maize straw (Rennert et al., 2008) with Al ions adsorbed.

DOM and DOM analysis

The DOM solution used to produce the coprecipitates and flocs mentioned in the previous section was taken from irrigation experiments conducted in our lab. Here, cylinders containing the O and EA horizon of an Albic Podzol (Arenic) were irrigated with synthetic rainwater (Krettek et al., 2022), and we merged eluates for the experiments of this study. The composite solution was filtered to 0.45 µm (nitrocellulose membrane). Its concentration of dissolved organic carbon (DOC) was 424 mg L^{-1}, analyzed by catalytic high temperature combustion (DIMATOC 2100; Dimatec), and Al (6 mg L^{-1}), Fe (13 mg L^{-1}), and Si (11 mg L^{-1}) concentrations were determined by microwave plasma-atomic emission spectrometry (MP-AES; 4200 MP-AES, Agilent). Molar absorptivity of DOM (SUVA) was calculated by dividing the absorption at 254 or 280 nm, determined by UV/VIS spectrophotometry (Cary 50, Varian; cuvette with 1 cm path length), by the molar DOC concentration, indicating high abundance of aromatic DOM ($SUVA_{254}$ = 775 L mol^{-1} cm^{-1} and $SUVA_{280}$ = 558 L mol^{-1} cm^{-1}).

Synthesis and characterization of SROAS and coprecipitates

We synthesized an Al-rich and a Si-rich SROAS (initial molar Al:Si ratio = 2 and 1) by neutralizing aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$; AppliChem) with sodium orthosilicate (Na_4SiO_4; abcr) according to Lenhardt et al. (2021). Two coprecipitates were produced from the same Al- and Si-sources (c($AlCl_3$) = 3.8 mmol L^{-1}; Al:Si = 2) by neutralization in the presence of DOM (Al:C = 0.5 or 2) to pH 6.5 within approximately 30 min at a rate of 0.1 mol OH^- mol^{-1} Al^{-1} min^{-1} (Lenhardt et al., 2022). Coprecipitates and the remaining supernatant after decanting were dialyzed for 20 h with a cellulose membrane (molecular weight cut-off 6–8 kD; Spectra Por 7, Repligen) to remove non-reacted species such as dissolved Na, Cl, and Si.

We determined the mass concentration of SROAS and coprecipitates gravimetrically by drying of 5–10 mL at 105°C in duplicate. Element contents were determined by dissolving SROAS and coprecipitates in 0.1 M HCl and quantification of Al, Si, Fe, and DOC as described before. Transmission infrared spectra of freeze-dried SROAS and coprecipitates were measured from KBr pellets prepared with a hydraulic press (1 mg of sample, 200 mg of KBr; Vertex 70, Bruker). Background scans were measured against the atmosphere before sample analysis (64 scans each). We added aliquots of SROAS and coprecipitate suspensions to silt-sized quartz (Millisil, Quarzwerke

GmbH) to avoid formation of large aggregates by drying (Lenhardt et al., 2021). Aluminum contents of the mixtures were adjusted to 2% on a dry mass basis. The mixtures were concentrated at 40°C and subsequently freeze-dried.

Synthesis and characterization of organic metal-containing species

Aluminum-organic and Fe-organic flocs were prepared by adding aliquots of a 0.2 M $AlCl_3$ or Fe chloride ($FeCl_3$; Carl Roth) solution to 150 mL of DOM solution and subsequent neutralization with 0.05 M NaOH. Initial Al and Fe concentrations were 1.75 mM, corresponding to an initial metal (Me):C ratio of 0.05. Solutions were neutralized at a rate of 0.1 mol OH^- mol^{-1} Me^{-1} min^{-1} to pH 3.5 (Fe variant) or pH 4.5 (Al variant; Jansen et al., 2003). Aliquots of the suspensions were pipetted into 50 mL polyethylene (PE) bottles in triplicate and centrifuged at 2120 *g*. The supernatants were decanted, and the bottles containing flocs were stored until the extractant was added. We determined Al, Fe, and DOC concentrations prior to neutralization and in the supernatants as described above. We calculated the amount of metals in the flocs and the Me:C ratios by difference, taking the volume of NaOH added into account. Freeze-dried flocs were analyzed by infrared spectroscopy as described above.

To prepare a model of particulate organic matter (POM) with Al ions adsorbed, charred maize straw was suspended in deionized water, and the pH was adjusted to <3.5 with HCl (10%). Subsequently, the charred straw was washed twice to remove desorbed cations (final electrical conductivity was 80 µS cm^{-1}) and dried at 105°C. We have chosen charred material, as it contains reactive functional groups for metal adsorption and has a low point of zero charge (e.g., Lian & Xing, 2017). Three grams of dried material were suspended in 200 mL of deionized water, dissolved $AlCl_3$ was added to achieve c = 30 µmol L^{-1}, and the pH was adjusted to 4. The low Al concentration was chosen to avoid polymerization of Al and precipitation of solids (checked by speciation calculations using Visual MINTEQ 3.1 [Gustafsson, 2020]). After shaking for 20 h, the charred straw was separated by filtration (0.45 µm). Adsorption of Al was quantified by the difference between initial Al concentration and that in the filtrate by MP-AES. The water content of the charred straw was determined gravimetrically after drying at 105°C to quantify dissolved Al retained in the filter.

Extraction of Al and Fe from model compounds by citrate

Model compounds were extracted by CIT according to Reyes and Torrent (1997). About 800 mg (dry mass; filtered charred straw was moist) was filled into 50 mL PE bottles, and 40 mL of a 0.2 M Na-citrate solution (pH adjusted to 6 with concentrated HCl) added. After horizontal shaking for 16 h at 180 rpm and centrifugation for 5 min at 1500 *g*, the aqueous phase was separated by filtration (0.45 µm). Concentrations of Al, Fe, and Si in the extracts were quantified by MP-AES and balanced with the respective amounts in model compounds (Table 1). We applied seven-point calibrations (Al and Fe 0–30 mg L^{-1} and Si 0–10 mg L^{-1}). Standard solutions with known concentrations were regularly analyzed together with the extracts.

TABLE 1 Composition of model compounds used for extraction with citrate at pH 6 and percentage of elements extracted.

	Al:Si	Me:C	Al	Si (%)	Fe
Si-rich SROAS	1.5	–	94.7	85.5	–
Al-rich SROAS	3.2	–	2.4	2.3	–
Coprecipitate	2.5	1.8	100	100	–
Coprecipitate	2.7	0.5	100	100	–
Al-OM flocs	–	0.05	100	–	–
Fe–OM flocs	–	0.05	–	–	100
Charred straw with adsorbed Al	–	–	100	–	–

Note: Al:Si and Me:C give the molar ratios of elements prior to citrate extraction (Me = Al or Fe).
Abbreviation: SROAS, short-range ordered aluminosilicate.

2.2.2 | Results

The synthesized SROAS had final Al:Si ratios of 1.5 and 3.2; hence, they were classified as Si-rich and Al-rich SROAS, respectively (Levard & Basile-Doelsch, 2016). Aluminum-rich SROAS resembled short-range ordered proto-imogolite with locally defined Si environments (Si in $Q^0$3Al configuration, i.e., a single Si tetrahedron is linked to three Al octahedra), as deduced from an infrared absorption band at 345 cm^{-1} (Figure 1a; Lenhardt et al., 2021). Silicon-rich SROAS contained more ill-defined Si species, evinced by a broad absorption band at 1000 cm^{-1} and absorption of silanol groups at 430 cm^{-1} (Figure 1a; Lenhardt et al., 2021). Given the lack of their characteristic IR absorption bands (Figure 1a), we exclude the formation of Al hydroxides during SROAS synthesis. The varying SROAS structures very likely caused the strong differences in CIT-extractable Al and Si (Table 1). While minor amounts were released from Al-rich SROAS (2.3% and 2.4% of total Si and Al, respectively), Si-rich SROAS was almost completely dissolved (85.5% [Si] and 94.7% [Al]). Natural SROAS from a volcanic deposit (Kaufhold et al., 2009) was dissolved by CIT to small extent (1.6% [Si] and 5.3% [Al]; Rennert et al., 2021). Based on the Al:Si ratio of 1.3, the natural SROAS would be classified as Si-rich allophane; however, infrared spectra indicated a pronounced contribution of polymerized octahedral Al together with a distinct signal of Si in $Q^0$3Al configuration (Kaufhold et al., 2009; Lenhardt et al., 2022). As the natural SROAS comprised naturally aged phases, it has very likely more spatial order than the fresh synthetic Si-rich SROAS from the current study. Our findings suggest that ill-defined, recently formed SROAS that has not undergone aging/alteration in natural environments may be readily dissolved during CIT extraction.

The Al:Si ratios (2.5 and 2.7) of the coprecipitates produced were larger than those of the initial solutions used for synthesis, as DOM hampers reactions between Al and Si (Lenhardt et al., 2022). The amounts of sorbed organic matter (Al:C ratios of 0.5 to 1.8; Table 1) differed because of varying initial DOM concentrations. Infrared spectra did not even indicate short-range order, as there was no signal of Si in $Q^0$3Al configuration close to 345 cm^{-1} (e.g., Lenhardt et al., 2022)

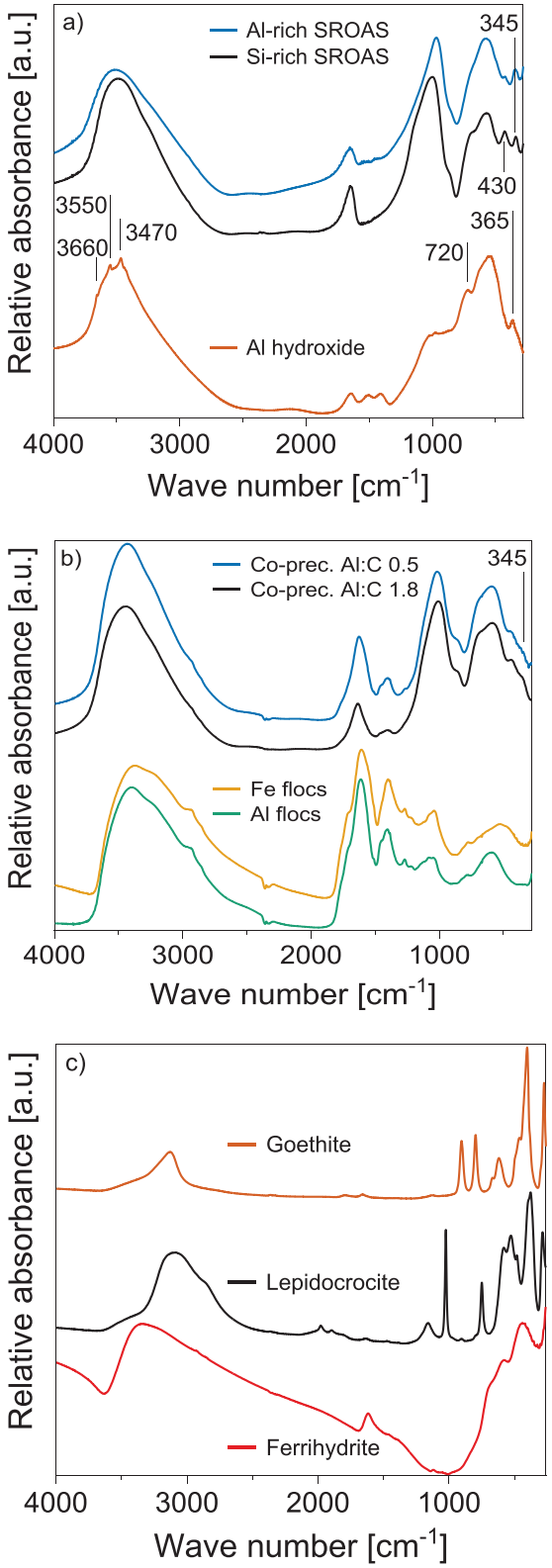

FIGURE 1 Transmission infrared spectra of (a) short-range ordered aluminosilicates (SROAS), poorly crystalline Al hydroxide, (b) coprecipitates (molar Al:C ratio 0.5 and 1.8) and Fe and Al flocs, and (c) Fe oxides. Spectra were normalized to absorption maxima at approximately 1000 cm^{-1} (SROAS and coprecipitates), 1600 cm^{-1} (flocs), 540 cm^{-1} (Al hydroxide), and 375–440 cm^{-1} (Fe oxides).

for both coprecipitates (Figure 1b). Both coprecipitates were completely dissolved by CIT extraction, releasing all Al previously present in organic association.

The Me:C ratio of both flocs formed by precipitating DOM with metals was low (0.05; Table 1). As the flocs formed at acidic pH with aromatic DOM, formation of amorphous Al hydroxide and ferrihydrite is unlikely (Chen et al., 2016; Jansen et al., 2003; Scheel et al., 2008). Concordantly, there were no signals of unintendedly formed phases in infrared spectra (Figure 1). These phases would include Al hydroxides (Figure 1a) and Fe oxides, but none of their characteristic infrared absorption bands (Figure 1c) was present in the spectra of the flocs (Figure 1b).

We detected rapid dispersion and dissolution of the flocs after adding the extractant even with the naked eye. Accordingly, Al and Fe were completely recovered in the extracts (Table 1). Adsorption of Al ions on charred straw was low (37 mg Al kg^{-1}) because of the low initial Al concentration. CIT extracted the adsorbed Al completely (Table 1).

Summarized, CIT was a complete extractant for Al and Fe in models of metal–organic associations, including coprecipitates of Al, Si, and DOM, organic flocs containing Al and Fe, and Al adsorbed on a model of POM. Similar to the partial dissolution of pyrite (15.7% of the total Fe; Rennert et al., 2021), CIT dissolved an analytical nontarget, here ill-defined SROAS so that extraction was not completely selective. However, the presence of both pyrite and ill-defined Si-rich SROAS is restricted to rather narrow pedogenetic conditions. Furthermore, the unintended dissolution of a naturally formed and aged Si-rich SROAS (Rennert et al., 2021) was distinctly below that of a poorly ordered SROAS, freshly synthesized for the current study.

2.3 | Time-dependency of extraction

Apart from completeness and selectivity discussed before, a further practical condition of any reliable extraction method is sufficient time to ensure complete extraction of the target species. As mentioned before, the extraction time of dithionite-based methods differs between Mehra and Jackson (1958), 15 min to max. 1 h, and Holmgren (1967), "overnight", whereas Varadachari et al. (2006) suggested 30 min plus time for cooling to room temperature with a dithionite-citrate method. Given the restricted time of the reduction capacity of dithionite (Section 2.1), the prolongation of extraction time would not ensure continual extraction. Instead, several authors recommended repeated extraction, that is, the solids to be extracted are separated from the original extractant solution and suspended in fresh extractant solution (e.g., Inda Junior & Kämpf, 2003; Mehra & Jackson, 1958; Thurman & Ciolkosz, 1992). The simple visible inspection of the sample after extraction is sufficient to decide on further extractions (Thurman & Ciolkosz, 1992). These are not necessary when the sample is no longer red or brown. Then, the statements on the completeness of dithionite-based extractions given in Section 2.1 apply.

Already the fundamental papers on Fe extraction by AOD (McKeague & Day, 1966; Schwertmann, 1964) revealed the time

dependency of Fe release. Schwertmann (1964) suggested 2 h extraction time. He also stated that any fixed period in the range of one to 5 h is random, although with progressive extraction more crystalline Fe oxides than the targeted X-ray amorphous ones were dissolved, but to unpredictable extent. Some poorly crystalline Fe oxides may be dissolved by Schwertmann's et al. (1964) method even after some minutes (Fischer, 1976). McKeague and Day (1966) suggested 4 h extraction for Al and Fe but designated this specification "somewhat arbitrarily". They reported asymptotically increasing extraction of Al and Fe from soil with increasing extraction time. However, McKeague and Day (1966) very likely did not study soil samples in which SROAS have predominantly accumulated, as Rennert and Lenhardt (2022) detected decreasing Al extraction with time from Andosol, Cambisol, and Podzol subsoil horizons, in which SROAS are known to form, although Al extraction from model SROAS increased with time. These authors concluded re-adsorption or precipitation of Al previously extracted in the presence of a soil matrix. These processes may explain why Kaufhold et al. (2010) designated the underestimation of allophane contents in soil by AOD extraction systematic. These results particularly contribute to the lack of selectivity and completeness of AOD-extractable Al mentioned in Section 2.1 in SROAS-containing soil.

A meaningful comparison of AOD-extraction data from different laboratories requires, inter alia (Section 2.4), identical extraction periods, or at least information on the extraction period. The first requirement is not even given for two frequently used soil classification systems, WRB and Soil Taxonomy. Extraction for 12 h was defined by Soil Taxonomy (Soil Survey Staff, 2014) until 2022, while 4 h can be used for WRB classification (IUSS Working Group WRB, 2022). Nowadays, the duration of extraction is 4–5 h with Soil Taxonomy (Soil Survey Staff, 2022b). Because of the expectable varying analytical results, varying classification of similar soils in both systems, for instance, Andosols/Andisols and Podzols, which require AOD data, seemed likely. Furthermore, 36 of the 49 papers that cited Schwertmann (1964) in 2022, according to scopus.com, did not provide information on the duration of extraction, which does not necessarily mean that the authors followed Schwertmann's suggestion of 2 h. The duration of extraction in the remaining 13 studies ranged from 2 and 4 h to "overnight".

The time dependency of CA and CIT extraction was checked by Reyes and Torrent (1997) and Gerke (1993), and it was considered in their extraction procedures. The completeness of CIT extraction after 16 h was confirmed in the current study (Section 2.2.2).

2.4 | Separation of the liquid extract from the remaining solid sample

All chemical extractions mentioned before rely on the transfer of Al and Fe from the solid phase of soil into the aqueous phase so that dissolved Al and Fe are subsequently analytically quantified by adequate techniques. This requires the complete separation of the liquid phase from the solid phase in a verifiable manner, but this does not always go without saying. None of the early extraction protocols of the still commonly used DCB and AOD methods (McKeague & Day, 1966; Mehra & Jackson, 1958; Schwertmann, 1964) provided precise and reproducible information on phase separation. Adequate and necessary information would include the pore size of filters used or the relative gravitational force during centrifugation, expressed as multiple of the earth's gravitational force *g*. Nowadays, dissolved species are operationally defined by the passage of a 0.45 µm filter (U.S. EPA, 1983).

Wagai and Mayer (2007) checked possible effects of centrifugation on the release of C during dithionite extraction. There was no difference between centrifugation with 7800 and 40,000 *g*. Considering that C released during dithionite extraction has primarily originated from Fe oxides that were reductively dissolved, effects of phase separation of the extent of Fe extraction by dithionite do not seem to play a major role. Rennert and Lenhardt (2022) checked effects of phase separation (centrifugation at 2200 *g*; 0.45 and 2 µm filtration, respectively) on AOD extraction of Al, Fe, and Si from soil. Significant effects of phase separation were frequent, particularly between the different filter sizes. For instance, the amount of Al extracted by AOD was significantly smaller after 0.45 µm filtration than after centrifugation and 2-µm filtration, and previous centrifugation significantly decreased the amounts of Fe extracted by AOD in filtrates (2 µm). These authors checked information on phase separation given in studies that were published in 2020. Fifty of the 65 papers citing Schwertmann (1964) did not give any information on phase separation, and so did 36 of the 45 papers citing McKeague and Day (1966). Similarly, 42 of the 49 studies reporting results from AOD extraction according to Schwertmann (1964) published in 2022 did not provide any information on phase separation either. Consequently, even in most recent studies, practical details on duration (Section 2.3) and phase separation, which may severely affect analytical data on AOD extraction, are mostly not documented at all. The need for generalization of the procedures themselves and of comprehensive statements on both the duration of extraction and phase separation instead of exclusively referring to ambiguous original papers is obvious. Although Fe-oxide particles <0.45 µm do exist (e.g., Regelink et al., 2014; Vasyukova et al., 2012), 0.45 µm filtration, given its operational definition for dissolved speciation, may be the most practically and scientifically general specification for phase separation in any extraction in terms of meaningful comparability of data.

The need for specification of phase separation is most obvious with PYR extraction. Already Loveland (1988) emphasized that it is vital to state exactly how PYR extraction has been conducted and equally important to compare with care the data obtained by different methods, as PYR mobilizes nontarget particles in addition to dissolved metals from organic associations. The amounts of Fe and Al extracted vary with experimental conditions, including centrifugation, flocculation, or filtration of extracts (Shang & Zelazny, 2008). Release of particles is a function of soil aggregation and possible dispersion by the extractant, which is particularly given with PYR (Borggaard, 1988). Bascomb (1968) reported that a PYR extract after centrifugation at 415 *g* was "cloudy", but "clear" at 35,000 *g*. Relative to the clay fraction, the sediment after high-speed centrifugation was enriched in goethite

by a factor of four so that goethite particles remained in suspension when centrifuging the extract with less gravitational force. Then, particulate goethite Fe would be wrongly attributed to dissolved Fe ions that were released from organic sources. Similarly, McKeague (1967) observed strong release of particles by PYR and suggested centrifuging at 20,000 *g*. However, Higashi et al. (1981) concluded that even at centrifugation at 20,000 *g*, the total Al and Fe extracted by PYR did not exclusively originate from SOM. Wagai et al. (2013) suggested centrifuging the extracts at 40,000 *g*, followed by filtration (0.025 µm), as an effective measure to exclude particulate Al and Fe from the measured Al and Fe concentrations in PYR extracts. Although high-speed centrifugation combined with 0.025 µm filtration surely improves the selectivity of PYR extraction by excluding particulate Al and Fe, the problems of poorly known completeness of PYR extraction of metals in organic association and release of Al from silicates at alkaline pH remain. We can only speculate whether these challenges connected to phase separation, completeness, and selectivity have provoked that PYR extraction is no longer used for the definition of the spodic horizon by Soil Taxonomy (Soil Survey Staff, 2022a). Anyway, PYR-extractable Al and Fe contents are no longer criteria for soil classification according to the recent editions of Soil Taxonomy and WRB (IUSS Working Group WRB, 2022; Soil Survey Staff, 2022a).

3 | RECOMMENDATIONS TO CIRCUMVENT POTENTIAL PITFALLS

3.1 | General aspects

The previous short summary of the potential analytical problems with commonly used extraction methods affirms their operational nature and definition. The very first step of avoiding misinterpretation of analytical data is being aware of the methods' potentials and limitations. An important limitation is that there is no completely selective extraction method to identify and quantify Fe-containing secondary minerals in soil (e.g., Borggaard, 1988; Rennert, 2019; Voelz et al., 2019). Consequently, we recommend following the suggestion by Voelz et al. (2019) to label, for instance, extracted Fe as a product of the extraction method, rather than as originating from a defined targeted phase (e.g., "oxalate-extractable Fe" rather than "Fe from ferrihydrite"). We suggest the same for Al.

Apart from this semantic, but nonetheless important recommendation, we consider several aspects that we propose in the following applicable to improve the reproducibility and thus the meaningfulness of data obtained by the extraction procedures mentioned before.

Even if PYR extraction is conducted with adequate phase separation, uncertainty remains, as further Al is dissolved from other than organic sources, and its completeness has not been comprehensively verified yet, as shown in Sections 2.1 and 2.4. We therefore suggest replacing PYR extraction by CIT extraction to characterize Al and Fe in soil, as (1) CIT is no dispersing agent like PYR, circumventing the problem of release of particulate Al and Fe and the necessity of sophisticated phase separation, (2) CIT extraction at pH 6 (0.2 M, 16 h extraction time) does not attack other primary and secondary minerals in soil, except for pyrite (Rennert et al., 2021) and unaltered ill-defined Si-rich SROAS, and (3) CIT extraction of Al and Fe from selected models of organic associations was complete (Section 2.2.2).

Furthermore, applying both CA and CIT extraction helps to identify the sources of Al and Fe in not-differentiable AOD extracts of soils, as differences calculated from the extracted contents provide information that is more detailed. For instance, $Al_{AOD} - Al_{CA}$ approximates Al in SROAS, as CA extracts Al from AOD-soluble forms except for SROAS (Rennert et al., 2021; Reyes & Torrent, 1997). Furthermore, Al and Fe present in poorly crystalline Fe oxides may be approximated by both $Me_{CA} - Me_{CIT}$ (Me = Al or Fe). This approach is restricted to poorly crystalline Fe oxides, as CA does not dissolve poorly crystalline Al oxides (Reyes & Torrent, 1997). Additionally, Fe in poorly crystalline Fe oxides may be approximated by $Fe_{AOD} - Fe_{CIT}$, as both AOD and CIT extract Fe from organic sources (Section 2.1). However, the approximation of Fe in poorly crystalline Fe oxides by these subtraction approaches may be biased by the different forms of Fe in organic associations mentioned in Section 2.1, amorphous organic flocs versus initially formed Fe-oxide crystallites embedded in an organic matrix. CIT does not dissolve synthetic poorly crystalline Fe oxides (Gerke, 1993; Rennert et al., 2021), but their dissolution by CIT when present as crystallites in an organic matrix (Section 2.1) is unknown yet.

As shown in Sections 2.1 and 2.3, AOD potentially extracts metals from a variety of forms, which partially even depends on the duration of extraction so that the interpretation of AOD data is associated with a potentially high degree of uncertainty, depending on the composition of the sample. As the combined application of CA and CIT extraction is a meaningful alternative, we suggest replacing the exclusive use of AOD by a combination of AOD, CA, and CIT extraction for soil characterization, classification, and survey. Random definition of thresholds, for instance, AOD data for the definition of the spodic horizon and andic properties based on an uncertain extraction, no longer seem appropriate when considering the available scientific literature. Meanwhile, more appropriate wet-chemical approaches for the quantification and characterization of poorly crystalline and organic Al and Fe species are available, which can be implemented in soil-science laboratories with similar effort as AOD extraction.

Irrespective of the subsequent use of extraction data, adequate interpretation of any extraction requires that several analytical criteria are met. These include:

- Using air-dried or freeze-dried samples, as particularly Fe oxides may be altered by oven-drying at 105°C. Instead, the water content of a batch of the soil sample is oven-dried at 105°C to relate the amounts of extracted elements to absolutely dry samples for comparison.
- Milling of samples prior to extraction, increasing the available surface area for reactions/exchange between the analytical target and the extractant.
- Extraction of replicate soil samples instead of only analytical replicates (i.e., the repeated analysis of a single extract of soil).

- Consideration of the analytical target(s) with AOD extraction, as effects of the duration of extraction differ between Al and Fe species (increasing Fe extraction, but possible re-adsorption of Al with time; Sections 2.3 and 3.2).
- Uniform and comprehensible phase separation. We strongly recommend following the operational definition of dissolved species, 0.45 µm, instead of individual and potentially subjectively defined centrifugation. In case of centrifugation, *g* needs to be provided with the results instead of rpm and duration.
- Quality control, that is, a thoroughly characterized soil is extracted together with all sets of unknown samples. Cumulative results of extraction of this reference soil give evidence of possible analytical problems and are thus a measure of reproducibility, as already suggested by Webber et al. (1974) for the commonly used extractions discussed in this paper. Analytical accuracy could be determined by extracting a mixture of model compounds with known metal speciation, for instance, adsorbed, coprecipitated, or flocculated. This, however, would require large-scale production at constant and controlled quality, and we suggest distribution of these model substances by an (inter-)national soil-science society, similar to clay minerals distributed by the Clay Minerals Society.
- Good laboratory practice, that is, regular calibration of the technique used for quantification, for instance, atomic absorption or atomic emission spectrometry. This includes the analysis of standard solutions with known concentrations together with the extracts.
- Finally, any reasonable comparison of extraction data between laboratories or published data implies identical analytical approaches among the studies, as shown by Loveland (1988) for PYR extraction.

Of course, these recommendations do not exclusively apply to extraction of Al and Fe from secondary soil constituents but also to that of other elements. Extraction of Si, the third important element in pedogenic forms apart from Al and Fe, is similarly multifaceted, as recently reviewed by Schaller et al. (2021). Apart from these general recommendations, recommendations that are more specific may apply (Table 2; Section 3.2).

3.2 | Specific recommendation for individual extractions

3.2.1 | Dithionite-based extractions

When applying the Mehra and Jackson (1958) method, a slight decrease in the original extraction temperature (80°C) is recommended, that is, a maximum of 75°C. This temperature reduces the formation of elemental sulfur and sulfides as well as decomposition of dithionite during extraction (Pansu & Gautheyrou, 2003). Heating during extraction following Mehra and Jackson (1958) is preferably carried out using a water bath and magnetic stirring. Solid Na dithionite (1 g) is added once the temperature of the suspension of soil in citrate-bicarbonate solution (40 mL of a 0.3 M Na-citrateCIT solution + 5 mL of a 1 M $NaHCO_3$ solution) has reached 75°C. The citrate solution should be prepared daily.

Extraction at room temperature according to Holmgren (1967) is slower so that the duration is prolonged to 16 h. Blakemore et al. (1987) suggested, when applying the Holmgren (1967) method, suspension of soil in 50 mL of a 0.75 M Na-citrate-dihydrate solution, followed by addition of 1 g Na dithionite. The samples are shaken horizontally at approximately 100 rpm. To ensure the complete dissolution of ferric Fe in all dithionite-based methods, an excess of the reductant dithionite and the complexing agent citrate is necessary so that 1–5 g of soil, depending on its color, is applicable to ensure a soil-to-solution ratio in the range of 1:50–1:100. As pointed out in Section 2.3, the extraction should be repeated when the red/brown color of soil has not disappeared after extraction by separating soil from solution phases first and adding reductant and complexing agent once again.

3.2.2 | AOD extraction

Although the inappropriateness of AOD for selective identification and quantification of certain Al and Fe species and thus soil-forming processes, from which these pedogenic species have evolved, has been proven several times (Sections 2.1 and 2.3, and references therein), it is still widely used. It is not possible to give a generally valid recommendation for the duration of AOD extraction, as, depending on the composition of the sample, the dependency of the extent of extraction on the duration of extraction differs between Al and Fe (Section 2.3). The duration of AOD extraction of SROAS-containing samples should not exceed 2 h, if Al is the analytical target, as Al is removed from solution by the soil during longer extraction. AOD-extractable Si in the range >1 g kg^{-1} may be an estimate of the presence of SROAS and thus an indicator of the necessity of shorter extraction. Since both McKeague and Day (1966) and Schwertmann (1964) did not specify a defined duration of extraction between 1 and 5 h, caused by the fact that the species being dissolved vary during extraction, it is not possible to recommend a certain general duration. Therefore, particularly AOD extraction has an obvious operational, rather than chemically/mineralogically defined character, given the dissolution of more crystalline Fe oxides with increasing extraction time. As Fe in organic association, in poorly crystalline (X-ray amorphous) and in more crystalline oxides forms a smooth transition, quantitative, that is, complete and selective extraction is per se impossible, as the analytical target is diffuse and differs between soils. This is, in our opinion, the main argument to overcome the exclusive use of AOD extraction with its obvious weaknesses and to replace its exclusive use with a more productive approach like the combination of AOD, CA, and CIT extraction.

When applying AOD extraction alone, we recommend 4 h for Al and Fe with samples, in which metals in organic association and in Fe oxides make up the majority of metals in AOD extracts. In the case of SROAS-containing samples, 2 h of extraction apply for Al and 4 h for Fe. According to Parfitt and Childs (1988) and references therein, a

TABLE 2 Summarized properties of extractions discussed and selected specific recommendations for practical use.

	DCB	AOD	CA	CIT	PYR
Original analytical target	Fe in ferric oxides	Al and Fe in X-ray amorphous forms	Fe in poorly crystalline oxides	Al and Fe in organic association	Al and Fe in organic association
Unintendedly released	Some metals from silicates and organic forms	Difficult to define, as analytical target is manifold	Nothing known	Partial dissolution of pyrite; poorly crystalline Si-rich SROAS	Dispersed mineral particles; partially Al from silicates at high pH
Selectivity	Depending on the proportion of unintendedly released species present in the studied samples	Not completely tested and presumably poor, given the multitude of phases (partially) attacked	Tested; selective	Tested; only two unintendedly dissolved minerals known	Not comprehensively tested; depending on phase separation
Completeness (model substances)	Not generally complete	Unknown for all forms attacked	Proven	Proven for selected targets	Unknown for all forms potentially attacked
Pitfalls	Misinterpretation of the Al released (no crystalline Al oxides dissolved)	Often misinterpreted: considered selective for poorly crystalline metal oxides	None known	None known apart from incomplete selectivity	Often incomplete phase separation, as 40,000 *g* centrifugation and 0.025 µm filtration required
Recommendations	Repeated extraction depending on soil color	Combination with CA and CIT; 2 h extraction for Al, 4 h for Fe	Application according to Reyes and Torrent (1997)	Application according to Reyes and Torrent (1997)	To be replaced by CIT; or full study on selectivity/completeness

Note: Please check the text for full details.
Abbreviations: AOD, ammonium oxalate-oxalic acid in darkness; CA, citrate-ascorbate; CIT, citrate; DCB, dithionite–citrate–bicarbonate; PYR, pyrophosphate; SROAS, short-range ordered aluminosilicate.

soil-to-solution ratio of 1:100 is recommended, and horizontal shaking with approximately 100 rpm.

3.2.3 | CA and CIT extraction

We recommend following the protocols by Reyes and Torrent (1997) for CA and CIT extraction. They used a 0.2 M Na-citrate solution, the pH of which they adjusted to 6 with solid ascorbic acid (approximately 7.2–8.4 g per liter 0.2 M Na-citrate solution), resulting in an ascorbic-acid concentration of 0.043–0.048 M, for CA extraction. A soil-to-solution ratio of 1:50 is applicable. Rennert et al. (2021) used 800 mg of soil or mineral and 40 mL of the CA solution in 50 mL bottles. More than 15 mL headspace in the bottle should be avoided to exclude excessive oxidation of ascorbic acid (Reyes & Torrent, 1997). Samples are shaken horizontally for 16 h, which is sufficient to dissolve Fe oxides as crystalline as six-line ferrihydrite (Reyes & Torrent, 1997). CIT extraction is conducted analogously with a 0.2 M Na-citrate solution. The pH of the solution is adjusted to 6 by careful, dropwise addition of hydrochloric acid.

ACKNOWLEDGMENTS

Open access funding enabled and organized by Projekt DEAL.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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How to cite this article: Rennert, T., & Lenhardt, K. R. (2025). Potential pitfalls when using popular chemical extractions to characterize Al- and Fe-containing soil constituents. *Journal of Plant Nutrition and Soil Science*, *188*, 730–741.
https://doi.org/10.1002/jpln.202300268