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Tiron Dissolution Method Used to Remove and Characterize Inorganic Components in Soils

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ABSTRACT

Treatments using NaOH and Na₂CO₃ have been widely used to remove poorly crystalline and noncrystalline aluminosilicates and hydrous oxides of Si and Al. However, NaOH treatment is often too harsh and Na₂CO₃ treatment is usually too mild and must be repeated. Treatment using alkaline Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid [disodium salt], C₆H₄(NaO₂S₂)₂) was as effective as acid oxalate in the dissolution of allophane, imogolite, and poorly crystalline hydrous Fe oxides. In contrast to oxalate, Tiron effectively removed opaline silica, and the difference between extracted Si could be used to measure the amount of opaline silica. Unlike oxalate, Tiron dissolved little magnetite. As gibbsite is partially dissolved by Tiron, the rates of Al release by gibbsite (<2 μm) dissolution at different temperatures were used to estimate the gibbsite contents of soil clays containing this mineral. Generally, a single treatment with Tiron appears to be sufficient to mildly but effectively clean up samples for x-ray diffraction of crystalline minerals with amounts of extracted Si, Al, and Fe indicating the presence and quantities of poorly crystalline and noncrystalline aluminosilicates as well as hydrous oxides of Fe, Al, and Si, including opaline silica.

THE CHARACTERIZATION of poorly crystalline and noncrystalline inorganic soil components is of considerable interest in view of their strong influence on the physical, chemical, and biological activities of soils. Chemical extractions are prerequisite for re-

moving these components from crystalline components and determining their overall composition.

In the past 80 yr, a number of chemical dissolution methods have been proposed, modified, and improved. Based on chemical reagents used and chemical reactions involved, these methods can be classified into one or more of the following four categories: (i) alkaline, (ii) acid, (iii) complexing, and (iv) reducing. Table 1 shows some major methods classified in these categories. The extraction capacity and selectivity of these dissolution methods are closely related to the mineral components to be extracted (Kodama and Jaakkimainen, 1982). For best efficiency, therefore, it is essential to select the dissolution method(s) appropriate to the components to be extracted.

Poorly crystalline and noncrystalline inorganic components in soils are mainly hydrous oxide compounds of Si, Al, and Fe (Mn) and hydrous aluminosilicates such as allophane and imogolite. Table 2 lists these minerals with some of their characteristics. Among the many dissolution methods summarized in Table 1, NaOH, Na₂CO₃, oxalate, and dithionite-citrate are perhaps most frequently used to remove the hydrous oxide and aluminosilicate minerals listed in Table 2. Hydroxylamine and Tiron are also applied, but less frequently. Since the Tiron method was originally proposed by Biermans and Baert (1977), it has been extensively applied in our laboratory (Wang et al., 1981; Kodama and Jaakkimainen, 1982; McKeague et al., 1983; Wang et al., 1986; Kodama and Wang, 1989; Kodama et al., 1989). This is because we have found

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Abbreviations: AA, atomic absorption; DCB, dithionite-citrate-bicarbonate; XRD, x-ray diffraction.

Table 1. Major chemical dissolution methods.

Category	Chemical reagents used for dissolution	Selected references
Alkaline	NaOH	Foster (1953) Hashimoto and Jackson (1960)
	Na ₂ CO ₃	Mitchell and Farmer (1962) Follet et al. (1965)
Acid	HCl	Deb (1950)
Alkaline plus acid	NaOH/HCl	Segalen (1968)
Complexing	H ₂ C ₂ O ₄	Chester and Hughes (1967)
	H ₂ C ₂ O ₄	Ball and Beaumont (1972)
	(NH ₄) ₂ C ₂ O ₄ /H ₂ C ₂ O ₄	Tamm (1922) Schwertmann (1959)
	Na ₂ C ₂ O ₄ /H ₂ C ₂ O ₄ C ₆ H ₄ Na ₂ O ₆ S ₂ (Tiron) Na ₃ P ₃ O ₇	Henmi and Wada (1976) Biermans and Baert (1977) McKeague (1967)
Reducing	NH ₂ OH·HCl/HCl	Chao and Zhou (1983)
Reducing plus complexing	Na ₂ C ₂ H ₂ O ₇ /NaHCO ₃ / Na ₂ S ₂ O ₄	Mehra and Jackson (1960)
	K ₂ C ₂ O ₄ /H ₂ C ₂ O ₄ /Mg (NH ₄) ₂ C ₂ O ₄ /H ₂ C ₂ O ₄ / Na ₂ S ₂ O ₄	Jeffries (1946) Duchauffour and Souchier (1966)

distinctive merit in this method, including a high efficiency equivalent to that obtained by a combination of other extraction methods. Therefore, several extraction procedures may simply be replaced by a single extraction with Tiron. The objective of this study was to compare Tiron and other common extraction methods on a wide variety of materials.

MATERIALS AND METHODS

A wide variety of crystalline, poorly crystalline, and non-crystalline minerals were selected to test the suitability of Tiron as an extractant for Si, Al, and Fe. Selected soil samples were also employed to provide examples of practical

application. The sources of these reference minerals and soil samples are listed in Table 3. The materials to be fractionated were suspended in water and the clay fractions (< 2 μm) were separated by a sedimentation method without centrifugation (Jackson, 1968). The pretreatment with H₂O₂ to destroy organic matter was applied only to soil samples, allophane, and imogolite prior to suspension. Fractionated clay fractions of five soil samples were saturated with Mg²⁺ and freeze-dried. The clay fractions of other samples were not saturated with Mg²⁺ before freeze-drying. For consolidated samples such as hematite, magnetite, goethite, gibbsite, lepidocrocite, opal, and obsidian, the mineral samples were first crushed to sand size and pure mineral grains were selected by handpicking.

After pulverizing by a Spex Mixer/Mill (Spex Industries, Metuchen, NJ), powdered samples were passed through a 50-μm nylon sieve. When further fractionation was required, as in the case of gibbsite, goethite, and hematite, the samples were suspended in water and fractionated using a sedimentation method without centrifugation. The fine-silt (2–5 μm) and clay (< 2 μm) fractions were freeze-dried. All other fractionated samples were dried at 60 °C in an oven. The ground silicate minerals were prepared by dry grinding for 96 to 180 h using a mechanical grinder. This procedure was followed to obtain partially noncrystalline specimens of known compositions (Kodama and Jaakimainen, 1982). Before use, the ground samples were dried overnight at 110 °C in an oven. Synthetic materials and two ferrihydrite samples were used as obtained or received, since they were already in a fine powdery state.

The Tiron method used in this investigation was modified from the method originally proposed by Biermans and Baert (1977). Detailed procedures are as follows. First 31.42 g of Tiron (Sigma no. D-7389, Sigma Chemical Co., St. Louis, MO) was dissolved in approximately 800 mL of H₂O in a plastic beaker. The resulting solution was acidic (pH ≈ 5.5) and light brownish yellow. A 100-mL Na₂CO₃ solution containing 5.3 g of anhydrous Na₂CO₃ was prepared in a plastic beaker and added to the Tiron solution while stirring. The

Table 2. Poorly crystalline and noncrystalline minerals occurring in soils.

Mineral	Idealized chemical formula	Structural characteristics and parameters	Characteristics		Reference
			X-ray diffraction pattern	Electron microscopic	
Opaline Silica	SiO ₂ ·nH ₂ O	Amorphous	A major band with a maximum near 0.4 nm.	Mostly spherical particles with 0.1–0.85 μm diameter	1,2
Opal-A	SiO ₂ ·nH ₂ O	Amorphous	A major band near 0.4 nm with diffuse maxima at 0.2, 0.15 and 0.12 nm.	Mostly spherical particles with 0.1–0.85 μm diameter	3
Opal-CT	SiO ₂ ·nH ₂ O	Amorphous plus poorly crystalline cristobalite and/or tridymite	A major band near 0.41 nm with minor bands corresponding to cristobalite and/or tridymite	Similar to opaline silica	3
Ferrihydrite	Fe ₂ O ₃ ·2FeOOH + 2.6H ₂ O	Rhombohedral a _c = 0.508 nm c = 0.94 nm	Broad peaks at 0.25, 0.22, 0.197, 0.171 and 0.15 nm.	Spherical	4
Feroxyhite (δ'-AlOOH)	FeOOH	Hexagonal a = 0.295 nm c = 0.453 nm	Broad peaks at 0.25, 0.22, 0.169 and 0.225 nm.	Acicular, possibly thin rolled plates	4
Wad	MnO ₂ ·nH ₂ O	Amorphous	A broad hump at 0.97 nm.	Platy, mostly irregularly outlined particles	5
Allophane	2SiO ₂ ·Al ₂ O ₃ ·nH ₂ O	Amorphous	Broad bands at 0.33 and 0.225 nm.	Hollow spherules or polyhedrons with diameter of 3.5–5 nm	6,7
Hisingerite	2SiO ₂ ·Fe ₂ O ₃ ·nH ₂ O	Amorphous	Broad bands at 0.44, 0.26 and 0.15 nm.		8,9
Imogolite	SiO ₂ ·Al ₂ O ₃ ·2.5H ₂ O	Two-dimensional tabular structure b = 0.51 nm c = 0.84 nm	Major peaks (broad) at 1.6, 0.79, and 0.33 nm with less pronounced peaks at 0.56, 0.44, 0.37, 0.25, 0.21 and 0.14 nm.	Smooth and curved threads varying in diameter from 10 to 30 nm and extending several micrometers in length.	10
					11
					12

† 1—Lanning et al. (1958); 2—Jones et al. (1964); 3—Levin and Ott (1933); 4—Carlson and Schwertmann (1980); 5—Hariya and Harada (1957); 6—Wada (1977); 7—Yoshinaga and Aomine (1962); 8—Sudo and Nakamura (1952); 9—Kohyama and Sudo (1975); 10—Yoshinaga (1968); 11—Cradwick et al. (1972); 12—Bayliss (1987).

pH of the Tiron solution rose to about 10.2 and the color of the solution turned greenish. Increments of 0.1 to 0.2 mL of 4 M NaOH were added until the pH reached 10.5 (according to our experience, about 23.5 mL of 4 M NaOH may

Table 3. Source of natural and synthetic reference minerals and selected soil samples.

Aluminum hydroxides	
Gibbsite	Richmond, Massachusetts, USA
Boehmite (synthetic)	Alcan Co.
Pseudoboehmite (synthetic)	Land Resource Research Centre (LRRC), Ottawa
Noncrystalline "Al(OH) ₃ " (synthetic)	LRRC, Ottawa
Iron oxides and hydroxides	
Hematite	Iron ore mine, Quebec, Canada
Maghemite, (synthetic)	Energy, Mine and Resources Canada
Magnetite	Ishpeming, MI
Goethite	Biwabik, MN
Akaganéite (synthetic)	LRRC, Ottawa
Lepidocrocite	Giessen, Germany
Ferrihydrite (S5)	Supplied by Drs. Schwertmann and Murad
Silicates for ground samples	
Kaolinite	Macon, GA
Biotite	Bancroft, Ontario, Canada
Microcline	Perth, Ontario, Canada
Fe-clinocllore	Chester, VT
Mg-hastingsite	Faraday, Ontario, Canada
Poorly crystalline hydrous silica and aluminosilicates	
Opaline silica (synthetic)	Silica gel, Fisher's Chemical reagent
Opal	Arizona
Opal	Hawaii
Obsidian	Little Lake, CA
Allophane	Kanuma, Tochigi, Japan
Imogolite	Kurayoshi, Tottori, Japan
Selected soil samples	
82-116, E horizon, Typic Cryorthods	Northern Québec pedon†
82-128, Bs2 horizon, Typic Cryorthods	Northern Québec pedon†
82-151, Bhs horizon, Typic Cryorthods	Northern Québec pedon†
84-2477A, E horizon, Typic Dystrochrept	Eastern Ontario pedon‡
7850, C3 horizon, saprolite-underlain Humic Haplorthod	Nova Scotia§

† Wang et al. (1986).

‡ Kodama and Wang (1989).

§ McKeague et al. (1983).

Table 4. Influence of the chemical composition of minerals on the extraction performance of various dissolution methods, as expressed by Al/Si and Fe/Si ratios of extracts.

Ground minerals	Original atomic ratio		NaOH			Na ₂ CO ₃			Tiron				Oxalate			Hydroxylamine							
	Al/Si	Fe/Si	Si	Al	Al/Si	Si	Al	Al/Si	Si	Al	Fe	Al/Si	Fe/Si	Si	Al	Fe	Al/Si	Fe/Si	Si	Al	Fe	Al/Si	Fe/Si
			— g kg ⁻¹ —			— g kg ⁻¹ —			— g kg ⁻¹ —				— g kg ⁻¹ —			— g kg ⁻¹ —							
Kaolinite (144 h)†	0.99	—‡	171	167	0.98	88	78	0.89	127	129	—	1.07	—	5	55	—	11.0	—	25	161	2	6.4	—
Microcline (160 h)	0.32	—	119	44	0.37	—	—	—	88	38	—	0.44	—	3	15	—	5.0	—	—	—	—	—	—
Biotite (180 h)	0.33	0.91	67	24	0.36	59	20	0.34	84	41	93	0.49	1.11	5	17	38	3.4	7.6	18	46	107	2.6	5.9
Fe clinocllore (132 h)	0.62	0.51	54	39	0.72	48	19	0.40	113	79	62	0.70	0.55	2	18	17	9.0	8.5	32	82	69	2.6	2.2
Mg hastingsite (96 h)	0.29	0.61	27	7	0.33	—	—	—	73	19	48	0.26	0.66	3	14	29	4.7	9.7	—	—	—	—	—

† h = grinding hours.

‡ Not determined.

be required). The total volume of the Tiron solution was then made up to 1 L. After standing for ≈0.5 h, the solution changed its color from greenish to light brownish yellow. The pH was adjusted to pH 10.5 since it may drop during storage. The solution was stored in a polypropylene container and kept in a refrigerator, allowing it to be used for up to about 3 mo without a noticeable decline of its extraction capacity. For extraction, 25 mg of a dry specimen was weighed in a 50-mL polypropylene centrifuge tube; 30 mL of the Tiron solution was then added to the tube and weighed. (Larger samples may be used in the same solid/solution ratio in larger containers.) The tube was covered loosely with a polypropylene cap, and placed in a water bath at 80 °C for 1 h. During the course of extraction, the contents were occasionally stirred by shaking manually. At the end of the 1-h extraction, the tube was cooled in a cold-water bath, the cap removed, the outside of the tube dried, and the contents weighed. Water was added according to weight loss due to evaporation. The contents were well mixed and centrifuged for 10 min at 17 600 g. A 20-mL sample of the supernatant was siphoned off for analysis of extracted Si, Al, and Fe by the AA spectrophotometric method. It has been proven in our laboratory that a reliable analysis can be obtained with or without destruction of Tiron prior to AA analysis. If Si in the supernatant is below the detection limit of the AA method, a colorimetric method must be applied after destroying Tiron by treating with 30% (w/w) H₂O₂ in a water bath until the color disappears. In this study, an autoanalyzer method (Technicon Autoanalyzer II) using molybdate (Wang and Schuppli, 1986) was employed to determine Si in the extracts after the destruction of Tiron.

For comparison, the following selective chemical dissolution methods were also employed: NaOH (Hashimoto and Jackson, 1960), Na₂CO₃ (Follet et al., 1965), ammonium oxalate (Schwertmann, 1959), sodium oxalate (Higashi and Ikeda, 1974), DCB (Mehra and Jackson, 1960), and hydroxylamine (Chao and Zhou, 1983; Ross et al., 1985).

X-ray diffraction analysis was done on oriented specimens using an automated Scintag PAD V diffractometer (Scintag, Sunnyvale, CA) with Co radiation and a graphite monochromator. Oriented specimens were prepared by drying a 1-mL water suspension containing 30 mg clay on 30- by 25-mm glass slide.

RESULTS AND DISCUSSION

Dissolution Selectivity

To distinguish between crystalline and noncrystalline substances, a method should selectively dissolve the noncrystalline portion only. In addition, the chem-

ical composition of noncrystalline substances should not influence the extraction performance of the method. To test for such an influence on dissolution methods, Al/Si and Fe/Si ratios of extracts from the ground silicates were compared with those of the original materials (Table 4). The DCB method was not used in this comparison, because this method has a specific selectivity for Fe and extracts noncrystalline and crystalline free Fe oxide compounds. As far as Al and Si proportions are concerned, the NaOH method worked well for the five mineral compositions. The results also show that NaOH has a high extraction capacity for Si and Al from Si-Al minerals such as kaolinite and microcline (Table 4). Recently, Kodama et al. (1989) suggested that the high amounts of Si and Al extracted from ground kaolinite might have been due to attack of NaOH on residual crystalline kaolinite. The extraction by Na_2CO_3 showed a trend similar to that by NaOH, but the extraction capacity of Na_2CO_3 was less than that of NaOH, although the Na_2CO_3 treatment was repeated three times. Oxalate and hydroxylamine showed a specific selectivity for Al and Fe; consequently, Al/Si and Fe/Si ratios of extracts were much higher than anticipated. The Tiron method showed balanced capability in extraction capacity and selectivity for the mineral compositions tested (Table 4). From these data, it is evident that all extraction methods except the Tiron method generally require at least one more complimentary extraction method to obtain reliable data for an overall composition of noncrystalline substances commonly consisting of Si, Al, and Fe. Shortcomings of the methods other than the Tiron method may be explained by the pH of the extraction media. No Fe is extractable at the high pH of the NaOH and Na_2CO_3 solutions, whereas very little Si is extractable at the low pH of the oxalate and hydroxylamine.

Cleaning Up Crystalline Minerals

There are always some less crystalline substances associated with clay-size crystalline minerals, and these substances are susceptible to selective chemical dissolution. This raises the question of where to draw the line between well and poorly crystalline substances. The distinction may depend on the chemical dissolution method applied. In general, it is preferable to avoid attack on crystalline substances by the chemical reagents used.

Figure 1 gives an example of how the alkaline Tiron method effectively cleaned up soil clay samples. The sample, pretreated with H_2O_2 and deferrated with dithionite-citrate, contained 5.18% Si, 10.05% Al, and 0.87% Fe, which were extractable by Tiron. A 1.4-nm mineral, quartz, and albite were barely recognized in the sample before extraction with Tiron. After Tiron extraction and subsequent saturation with Mg^{2+} , an amphibole mineral and microcline as well as quartz and albite were definitely identified. With glycerol and heat treatment, the 1.4-nm mineral was identified as vermiculite. It is evident that Tiron removed coating and cementing agents to disintegrate aggregates and expose more cleaned mineral particles. The drastic improvement in the XRD patterns can be attributed to better orientation of phyllosilicates and more exposure of other silicates, as well as to the increased concentration of crystalline components.

With the use of ammonium oxalate, there is the possibility that NH_4^+ might be fixed in expansible clay minerals, particularly in vermiculite, to cause structural contraction of these minerals. To avoid this possibility, Higashi and Ikeda (1974) proposed the use of sodium oxalate in place of ammonium oxalate. Coderre (1985, personal communication) illustrated the effect on vermiculite-bearing soil samples by comparing their XRD patterns before and after treatments with ammonium and sodium oxalate. Some of the ammonium oxalate treated samples showed an increase in the 1.0-nm peak intensity at the expense of the 1.4-nm peak intensity of the vermiculite component. Unlike the ammonium oxalate method, the Tiron method does not cause such structural alterations.

Dissolution of Poorly Crystalline Silicate and Aluminosilicate Minerals

The dissolution of poorly crystalline silicate minerals, allophane, and imogolite by Tiron was compared with the dissolution of these minerals by NaOH and oxalate (Table 5). Tiron extracted nearly as much Si from opaline silica as did NaOH, whereas oxalate extracted almost no Si from it. Since the opaline silica contained about $180 \text{ g H}_2\text{O kg}^{-1}$, the amounts of Si extracted by the two methods corresponded closely to the total amounts of Si from the opaline silica. Undoubtedly, the low pH (3.0–3.5) of the oxalate solution is the main reason for the low Si extraction. For the Arizona opal (opal-CT, Jones and Segnet, 1971), the

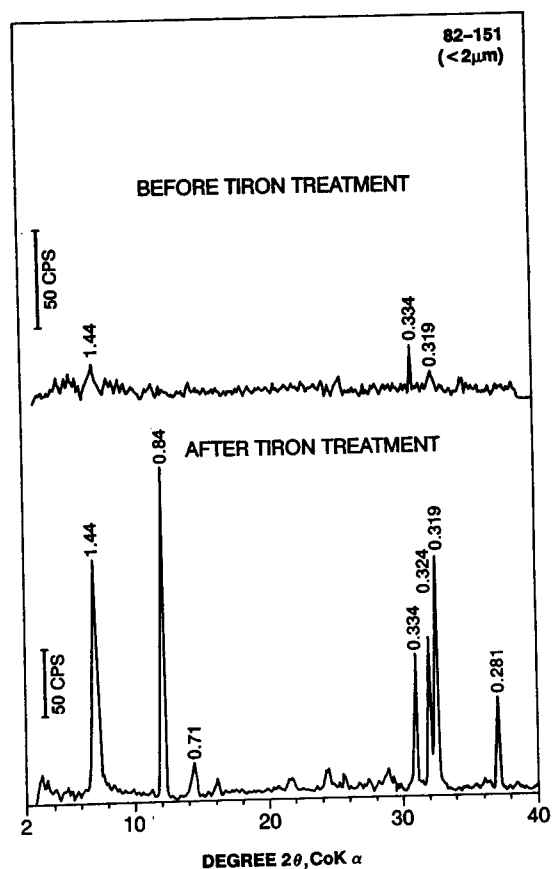


Fig. 1. X-ray diffraction patterns of a soil clay (82-151) before and after Tiron treatment (CPS: counts per second). Spacings are in nanometers.

Table 5. Amounts of major elements extracted from opaline silica, opal, allophane, and imogolite by three different chemical dissolution methods.

	NaOH		Tiron			Oxalate		
	Si	Al	Si	Al	Fe	Si	Al	Fe
	g kg ⁻¹							
Opaline silica	397	—	379	—	—	1	—	—
Opal, Arizona	278	tr†	38	tr	0	0	—	—
Obsidian, California	73	13	53	10	8	—	—	—
Opal, Hawaii	43	tr	50	0	tr	0	—	—
Allophane, Kanuma, Japan	—	—	114	165	50	115	163	53
Imogolite, Kurayoshi, Japan	—	—	73	103	12	68	96	14

† Trace.

Table 6. Amounts of Si, Al, and Fe extracted from surface soil samples by the Tiron and oxalate methods.

Sample (horizon)	Tiron			Oxalate			ΔSi†
	Si	Al	Fe	Si	Al	Fe	
82-116 (E)	1050	28	26	tr	13	25	1050
84-2477A (E)	1025	133	290	tr	89	294	1025

† ΔSi = Tiron-extracted Si minus oxalate-extracted Si.

amount of Si extracted by Tiron was substantially lower than that by NaOH. Besides these minerals, this opal sample contained pyroxene as an impurity. Only a fraction of Si from volcanic glassy substances such as obsidian and Hawaiian opal was extractable with NaOH and Tiron. Obsidians are essentially unhydrated silicate glasses that have a three-dimensional disordered framework structure. Therefore, very limited dissolution of the obsidian by alkaline solutions was anticipated. However, the results for the Hawaiian opal were not fully understood, since its XRD pattern with a single hump near 0.4 nm was typical of opal. One explanation is that the opal is composed of sub-microscopically crystalline silica substances that are still amorphous to x-rays because of extremely small crystallite size.

Dissolution of allophane and imogolite by Tiron was comparable to that by oxalate. Assuming that this allophane has a chemical composition similar to the one reported for an allophane from the same locality (Sudo, 1968), the amounts of Si and Al extracted indicate that both treatments dissolved almost all of the mineral. Similarly, Tiron and oxalate were also equally effective extractants for imogolite, which contained some quartz and feldspar.

Since Si is extracted from allophane and imogolite but not from opaline silica by oxalate (Si_o) and Si is extracted from all three by Tiron (Si_T), the difference (ΔSi = Si_T - Si_o) may be used as an indicator of the amount of opaline silica. This idea was tested on the clay fractions of surface soil samples. Table 6 gives two representative cases showing high ΔSi values, although amounts of Al and Fe extracted were comparable between the two dissolution methods. Differential XRD patterns (not shown) indicated the presence of a broad hump with a maximum near 0.39 nm, which is a characteristic feature of standard silica gel (Kodama and Wang, 1989). Therefore, this procedure appears to be a useful indicator of amounts of opaline silica.

Table 7. Amounts of Al extracted from hydrous Al oxide minerals by four different chemical dissolution methods.

Mineral	Origin	Amount of Al extracted			
		Tiron	Oxalate	NaOH	DCB†
		g kg ⁻¹			
Aluminum hydroxide (noncrystalline)	Synthetic	221	215	—‡	—
Pseudoboehmite	Synthetic	301	40	—	—
Boehmite	Synthetic	2	1	—	—
Gibbsite <2 μm	Richmond, MA	138	12	282	6
Gibbsite 2-5 μm	Richmond, MA	51	8	275	1
Gibbsite 5-20 μm	Richmond, MA	23	6	230	1
Gibbsite 20-44 μm	Richmond, MA	5	1	149	tr

† Dithionite-citrate-bicarbonate.

‡ Not determined.

Aluminum Hydroxide and Oxyhydroxide Minerals

Tiron and oxalate extracted nearly equal amounts of Al from noncrystalline synthetic hydrous Al oxide (Table 7). However, Tiron extracted far more Al from pseudoboehmite than did oxalate. Neither method attacked a well-crystalline boehmite. With fractionated gibbsite samples, there was a general effect of surface area on the amount of Al extracted, as amounts of extractable Al increased with a decrease in particle size. Compared with oxalate and DCB treatments, Tiron dissolved considerably more Al from gibbsite, particularly clay-size gibbsite. This indicated that Tiron partially dissolves gibbsite, confirming the finding of Biermans and Baert (1977). Therefore, if any soil samples containing clay-size gibbsite requires chemical dissolution treatment for cleaning up, the oxalate method should be applied. If oxalate treatment does not improve XRD patterns, the Tiron method may still be usable with the correction formula $K(m_2 - m_1)/(\alpha_2 - \alpha_1)$, where K is the conversion factor, 2.89, from Al to Al(OH)₃, m_1 and m_2 are the amounts of Al extracted by Tiron from a sample after a 1-h reaction at 60 °C and 80 °C, respectively, and α_1 and α_2 are the 1-h reaction rates of clay-size gibbsite at 60 °C and 80 °C, respectively. The α_1 and α_2 rates were predetermined from separate solubility experiments on clay-size gibbsite. The solubility of gibbsite increased exponentially with increase in temperature and time of reaction with Tiron (Fig. 2), and these solubility curves could be explained by a combination of first-order (up to 45 min) and two-dimensional diffusion-controlled (>45 min) reactions (Fig. 3). Since a 1-h reaction time at 80 °C was used as a routine extraction procedure, 60 °C was considered to be the appropriate choice for another temperature. Thus, from Fig. 2, α_1 (60 °C) = 0.28 and α_2 (80 °C) = 0.58. The correction formula can then be simplified to $9.63(m_2 - m_1)$. A working example is illustrated in Fig. 4. A saprolite from Nova Scotia required Tiron treatment to obtain improved XRD patterns from which crystalline components could be identified. The pattern before treatment showed only one peak at 0.483 nm, which corresponded to the strongest peak of gibbsite. After the treatment, several minerals including gibbsite were identifiable (Fig. 4). Tiron extracted 16.8 μg Al mg⁻¹

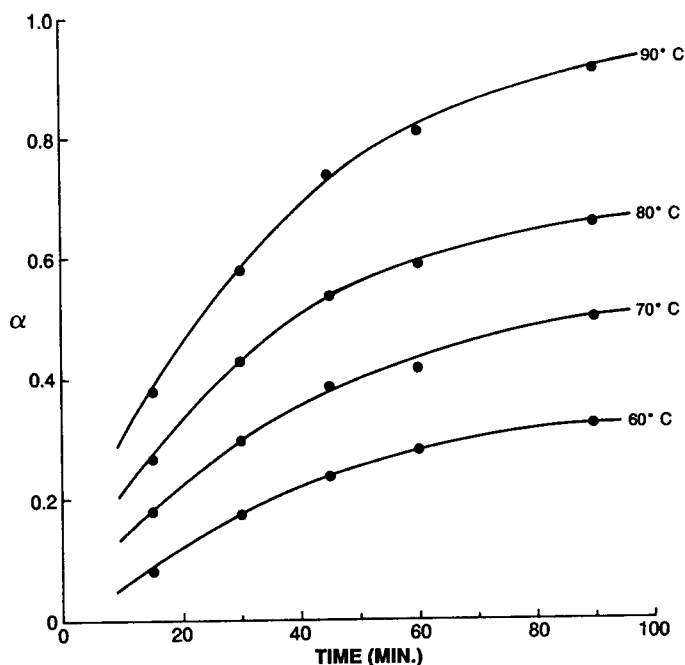


Fig. 2. Tiron dissolution curves represented by the fraction reacted, α , against time for a clay-size gibbsite at four different temperatures.

sample under the conditions for the routine procedure, whereas $5.8 \mu\text{g Al}$ was extracted after the 1-h reaction at 60°C . Therefore, the results indicate that the original sample contained about $105 \text{ g gibbsite kg}^{-1}$. This estimate was comparable with the amount determined by thermogravimetric and x-ray methods (McKeague et al., 1983).

Iron Oxide and Oxyhydroxide Minerals

The dissolution capacity of Tiron for ferrihydrite is similar to that of oxalate, although Tiron extracted somewhat less Fe than did oxalate (Table 8). For crystalline Fe oxyhydroxides such as goethite and lepidocrocite, the data of both treatments were in good agreement. With maghemite and hematite, the amounts of Fe extracted by oxalate, although small, were consistently much higher than those extracted by Tiron, perhaps due to the acidity of the oxalate solution. The most striking observation was that Tiron reacted very little with magnetite, whereas oxalate dissolved nearly 70% of magnetite. Chao and Zhou (1983) proposed an alternative method using hydroxylamine, which does not attack magnetite and other crystalline Fe oxides. Ross et al. (1985) and Wang et al. (1987) found that the hydroxylamine method gave a good approximation of oxalate-extractable Fe and Al of soil samples, and they proposed that the hydroxylamine method should be used for soils containing magnetite. Considering the results discussed above, Tiron also proved to be a more suitable reagent than oxalate, particularly for magnetite-bearing samples.

The DCB treatment is known to extract total free Fe. The effectiveness of dissolution, however, is greatly affected by the particle size of the crystalline Fe oxide minerals such as goethite and hematite (Table 8). The data clearly indicate that a single DCB treatment was not sufficient to dissolve even clay-size goethite (the-

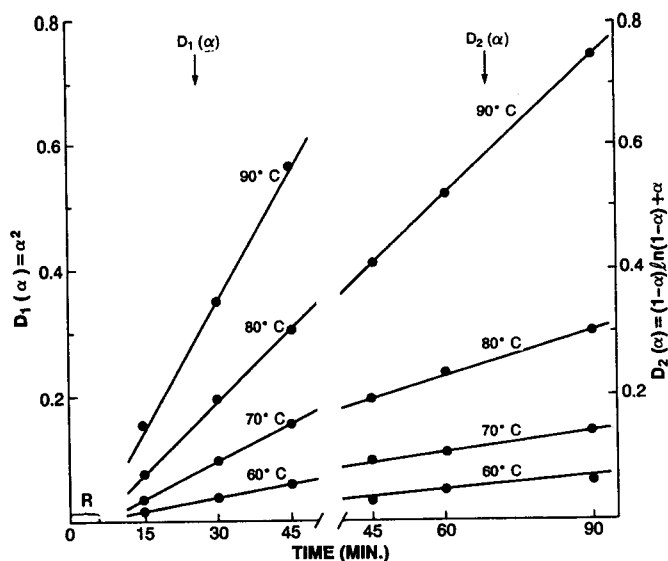


Fig. 3. Plots of first-order (D_1) and two-dimensional diffusion (D_2) reactions as a function of reaction rates (α) against time for the dissolution of $<2\text{-}\mu\text{m}$ gibbsite by Tiron at four different temperatures.

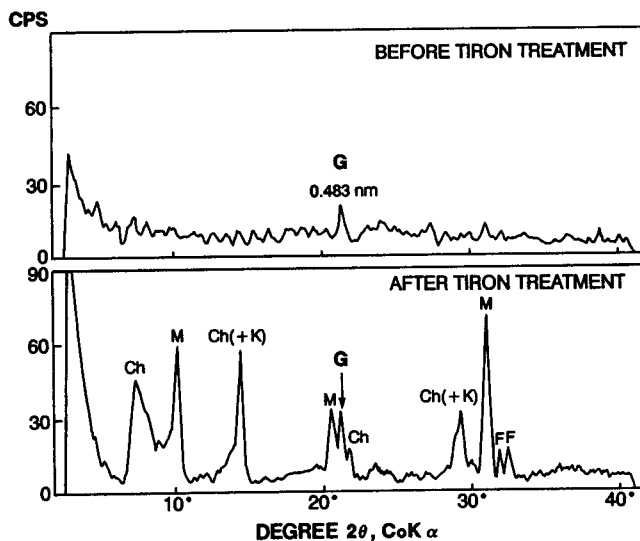


Fig. 4. X-ray diffraction patterns of a soil clay (7850) containing gibbsite (G) before and after Tiron treatment. Ch: chlorite, M: mica, K: kaolinite, F: feldspars.

oretically containing 629 g Fe kg^{-1}). Silt-size hematite (699 g Fe kg^{-1}) required >10 repeated extractions and only about 60% of its coarser silt-size hematite was dissolved after 19 extractions. These facts should be borne in mind when extraction data are analyzed in detail to estimate crystalline and noncrystalline Fe oxide components.

As additional information, it was found in our laboratory that both Tiron and oxalate extracted substantial amounts of Fe from siderite (FeCO_3 , $<44 \mu\text{m}$). Although it is not an Fe oxide mineral, it is occasionally found in soils and sediments. Tiron and oxalate extracted 157 g Fe kg^{-1} and 142 g Fe kg^{-1} , respectively, which corresponds to about $300 \text{ g FeCO}_3 \text{ kg}^{-1}$. In contrast, dithionite-citrate extraction at room temperature for 16 h liberated only 40 g Fe kg^{-1} from this mineral.

Table 8. Amounts of Fe extracted from Fe oxide and hydrous oxide minerals by three different chemical dissolution methods.

Mineral	Tiron	Oxalate	DCB†
	g kg ⁻¹		
Ferrihydrite-N163	417	474	—
Ferrihydrite-S5	363	403	—
Goethite <2 μm	12	15	582(1)‡
Goethite 2–5 μm	5	8	574(1)
Goethite 5–20 μm	2	5	545(1) 590(2)
Goethite 20–44 μm	0.5	tr	380(1) 582(6)
Akaganeite	32	17	—
Lepidocrocite <44 μm	9	10	—
Maghemite	6	17	—
Hematite 5–20 μm	0.4	37	204(1) 655(10)
Hematite 20–44 μm	0.1	29	37(1) 395(19)
Magnetite <44 μm	3	537	—

† Dithionite-citrate-bicarbonate.

‡ Number in bracket indicates number of treatments.

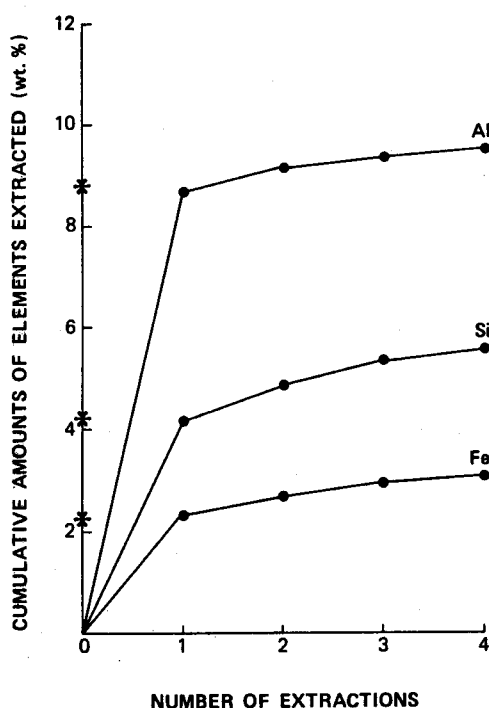


Fig. 5. Dissolution by Tiron of Si, Al, and Fe from a soil clay as expressed in cumulative amounts (percent by weight) for four successive treatments (* indicates projection of a straight line through the data points from the second, third, and fourth extractions on the Y axis).

Effectiveness of the Tiron Method

The cumulative amounts of Fe, Al, and Si extracted from a clay-size soil sample (82-128) by four repeated Tiron treatments indicated that nearly all the extraction occurred in the first treatment (Fig. 5). Extrapolation of a straight line through the data points from the second, third, and fourth extractions to zero extraction on the Y axis (marked by * in Fig. 5) shows that the extrapolated values are close to the amounts extracted in the first treatment. These and other unpublished data (1988) on a number of clay-size soil samples in Canada suggest that a single Tiron treatment is sufficient to dissolve Si, Al, and Fe or poorly crystalline and noncrystalline components in most soil clays.

CONCLUSIONS

1. Tiron treatment appeared to be more effective than NaOH treatment in removing the noncrystalline components from aluminosilicates without significantly attacking the crystalline components.
2. Tiron treatment was as effective as oxalate treatment in the dissolution of allophane, imogolite, and short-range-ordered hydrous oxides (e.g., ferrihydrite).
3. In contrast to oxalate treatment, Tiron treatment effectively removed opaline silica. The difference between the amounts of Si extracted by the two treatments could be used to measure the amount of opaline silica.
4. Unlike oxalate treatment, Tiron treatment dissolved little or no magnetite.
5. Generally, a single treatment with Tiron appears to be sufficient to clean up samples for XRD analysis of crystalline minerals. The amounts of extracted Si, Al, and Fe indicate the amounts of short-range-ordered aluminosilicates and hydrous oxides of Fe, Al, and Si.

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