

presence of Mg-Al-SiO₂ compounds of reduced solubility. Occurrence of these complexes of Mg have been pointed out by Eaton et al. (3) and Kardos et al. (6). The relatively high acid-soluble Mg in the soils indicates that the Mg-Al silicates dissolve upon boiling with 1N HNO₃. The presence of more exchangeable than acid-soluble Mg in the youthful alluvial soils from Southeast Asia (Cai San clay, Phu Hiep clay) apparently suggest that the concentration of the Mg complexes increases with the age of the soil.

Data presented in Table I also indicate that only a small fraction of total Mg, estimated at from 0.05 to 2.8%, occurred in organic-complexed forms. The data contradict the suggestion by Salmon (11) that Mg is held by organic matter in other than exchangeable forms. The data further suggest that Mg held by organic matter is readily releasable upon extraction with 1N NH₄OAc.

The Mg fractionation scheme presented here can be used to characterize Mg in soils that are different in origin or stage of development. The scheme can be used to study fixation of Mg added to soils by following its redistribution in the various soil forms. It can also be used to study the uptake of soil Mg by plants by determining the contribution of each form of the element to growing plants in a test soil, over a given period of time.

LITERATURE CITED

1. Beavers, A. H., W. D. Johns, R. E. Grim, and R. T. Odell. 1955. Clay minerals in some Illinois soils developed from loess and till under grass vegetation. *Clays Clay Miner.* 395(3):356-372.
2. Catherwood, M. P., and E. E. De Turk. 1929. The relation of soil type to the exchangeable Ca and Mg in some Illinois soils. *J. Amer. Soc. Agron.* 20:657-678.
3. Eaton, F. M., G. W. McLean, G. S. Bredell, and H. E. Donner. 1968. Significance of silica in the loss of magnesium from irrigation waters. *Soil Sci.* 105:260-280.
4. Jackson, M. L. 1956. *Soil chemical analysis—Advanced course* (Second printing, 1965). Published by the author, Dept. of Soil Science, University of Wisconsin, Madison, Wis.
5. Jackson, M. L. 1958. *Soil chemical analysis* (Fourth printing, 1964). Prentice Hall, Englewood Cliffs, New Jersey.
6. Kardos, L. T., and J. S. Joffe. 1938. The preparation, composition and chemical behavior of the complex silicates of Mg, Ca, Sr and Ba. *Soil Sci.* 45:293-308.
7. Odell, R. T., and J. C. Dijkerman. 1967. Properties, classification and use of tropical soils, with special reference to those in Sierra Leone. Njala University College, University of Sierra Leone.
8. Prince, A. L., M. Zimmerman, and F. E. Bear. 1947. The magnesium supplying power of twenty New Jersey soils. *Soil Sci.* 63:69-78.
9. Rice, H. B., and E. J. Kamprath. 1968. Availability of exchangeable and nonexchangeable magnesium in sandy Coastal Plain soils. *Soil Sci. Soc. Amer. Proc.* 32:386-388.
10. Rouse, F. D., and B. R. Bertramson. 1949. Potassium availability in several Indiana soils: Its nature and methods of evaluation. *Soil Sci. Soc. Amer. Proc.* 14:113-123.
11. Salmon, R. C. 1963. Magnesium relationships in soils and plants. *J. Sci. Food Agr.* 14:605-610.
12. Wascher, H. L., J. B. Fehrenbacher, R. T. Odell, and P. T. Veale. 1950. Illinois soil type descriptions. Dept. of Agronomy, University of Illinois, Agr. Expt. Sta.

Selective Dissolution of Manganese Oxides from Soils and Sediments with Acidified Hydroxylamine Hydrochloride¹

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ABSTRACT

Hydrous manganese and iron oxides of soils and sediments are strong scavenging agents for heavy metal ions. Information on heavy metals extracted along with manganese and iron oxides has been used in mineral exploration. But currently used methods do not differentiate metal ions associated with manganese oxides and those associated with iron oxides. Manganese oxides differ from iron oxides in solubility in response to oxidation-reduction conditions, charge characteristics, and the quantity and kind of metal ions scavenged. This paper reports the development of an extraction method for the selective dissolution of manganese oxides from soils and sediments with minimal attack on the coexisting iron oxides, based on the difference in behavior of manganese oxides and iron oxides toward reduction under various conditions. By dissolving manganese oxides and iron oxides separately and determining respective metal ions which are released in the process, the geochemical significance of interelement relationships may be established.

Manganese oxides in soils and sediments are found to be readily dissolved by a hydroxylamine hydrochloride (NH₂OH·HCl) solution, leaving the major part of iron oxides in the residue. Although dissolution of manganese oxides is relatively

independent of pH (pH 1, 2, and 3) and concentration of the NH₂OH·HCl solution (0.025 to 0.25M), and time of equilibration (15 to 60 min), progressively greater amounts of iron oxides are released with lower pH and higher concentration of NH₂OH·HCl solution, and with longer time of equilibration. A 0.1M NH₂OH·HCl solution prepared in 0.01M HNO₃ (pH 2) dissolves, on the average, 85% of manganese oxides and about 5% of iron oxides from various sediments after equilibrating for 30 min. Dissolution of manganese oxides and of iron oxides from four highly weathered soils by this solution amounts, respectively, to 50% and less than 1%. At pH 2, most heavy metal ions released during the dissolution of manganese oxides will be prevented from forming insoluble hydroxides or basic salts through hydrolysis, and then they can be determined in solution by appropriate analytical methods.

Additional Index Words: geochemical exploration, iron oxides.

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MANGANESE IN SOILS and sediments, under aerated conditions, exists principally as various oxides and hydrous oxides (21, 22, 25, 28). These secondary oxides, associated with iron oxides, generally occur as nodules and concretions, or as stains and coatings on surfaces of soil and sediment particles. In a recent study, Taylor et al. (31) identified the mineralogical structure of several polymorphs of manganese oxides isolated from soils, and gave chemical formulae for them.

Hydrous manganese and iron oxides are strong scavenging agents for transition metal ions and geochemists have applied to mineral exploration information on heavy metals extracted with manganese and iron oxides (4, 11, 13, 14). Manganese oxides differ from iron oxides in solubility in natural environment in response to oxidation-reduction conditions (16, 32), charge characteristics (12, 23, 26, 27), and the quantity and kind of metal ions scavenged (11, 15, 21, 23, 29, 30). The preferential adsorption of cobalt by manganese oxides (19) illustrates the latter. Nevertheless, few attempts have been made in the past to differentiate the two groups of oxides by developing a method that would selectively dissolve one group of oxides without seriously attacking the other. Several investigators (1, 2, 7) have used the dithionite reagent in one form or another, originally designed for the dissolution of free iron oxides, to extract manganese oxides from soils and clays. Le Riche and Weir (17) extracted iron oxides from soils with ammonium oxalate (pH 3.3) under ultraviolet light; however, this extractant also removed 84 to 95% of the manganese in the soils in addition to 62 to 69% of the total iron (30). Chester and Hughes (6) affected a combined dissolution of the iron oxide and manganese oxide phases of a ferromanganese nodule by equilibrating the sample with 1M hydroxylamine hydrochloride in 25% (v/v) acetic acid.

Any of these methods mentioned may, when used to extract heavy metals from soils or sediments, give ambiguous results, inasmuch as the extracted metals attributed to iron oxides may have actually resulted from the dissolution of manganese oxides and vice versa. Admittedly, interelement relationships may be directly established by electron microprobe analysis (3, 9), but equipment required for such measurements is not easily accessible to many investigators. Only recently have Taylor and McKenzie (30) reported utilizing a 10% hydrogen peroxide in 0.001N nitric acid to extract manganese oxides. However, this method requires prolonged peroxide treatment.

The above observations demonstrate the need for a more effective and rapid method to selectively dissolve manganese oxides from soils and sediments, with minimal attack on the coexisting iron oxides. This paper reports the development of an extraction method for the selective dissolution of manganese oxides from soils and sediments by acidified hydroxylamine hydrochloride, based on the difference in behavior of manganese and iron oxides toward reduction under various conditions.

MATERIALS AND METHODS

Thirty-three samples were used in this study. Nine sediment samples were collected from mineralized areas in west-central and southeast Maine, seven sediment samples from streams

draining mine dumps in central and southwest Colorado, and four soil samples from Hawaii classified as members of the low humic latosol group. Thirteen manganese oxides and iron oxides were either prepared in the laboratory or purchased from commercial sources.

The soil and sediment samples were ground to pass through a 100-mesh sieve, and then fused with a mixture of sodium carbonate and borax (24) for total manganese and iron determinations. Manganese oxides and iron oxides were dissolved by acid digestion for total manganese and iron determinations. For extraction, 0.10 to 0.50-g sample and 25 ml hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) solution of a certain concentration and pH were equilibrated on a mechanical shaker for a variable length of time. One series of sediment samples were extracted eight times in succession with a solution of 0.1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.1M HNO_3 , each time using fresh $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution. The suspension was then centrifuged and the supernatant solution taken for manganese and iron determinations. The analysis was carried out by atomic absorption with a 303 Perkin-Elmer spectrophotometer.

RESULTS AND DISCUSSION

Effect of $\text{NH}_2\text{OH} \cdot \text{HCl}$ Concentration, pH, and Extraction Time on Manganese Dissolution

The ability of hydroxylamine hydrochloride to dissolve iron oxides and/or manganese oxides in soils, sediments and plant ashes has been established by Dion et al. (8), Canney and Nowlan (5), Arrhenius and Kharkar (quoted by Lynn and Bonatti, 18), Chester and Hughes (6), and White (33). The present investigation studied such factors as concentration and acidity of the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution as well as time of equilibration so as to define optimum conditions for dissolving manganese oxides selectively without excessive concomitant attack on iron oxides.

Figure 1 shows the accumulative dissolution of manganese and iron from four of the sediment samples by eight successive extractions with 0.1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.1M HNO_3 (pH 1) after various intervals of time of equilibration. Most noticeable in the graph is the more rapid dissolution of manganese than iron. The first extraction, after 15 min of shaking, removed more than 70% of the total manganese, and then the dissolution of manganese leveled off with further extractions. Generally, about 80% of the total manganese of these samples exists as reactive manganese oxides which can be readily reduced and dissolved by the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution at pH 1. The remaining manganese, released slowly with further extractions, may be present as relatively unweathered primary minerals, or in forms not readily dissolved by the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution. This dissolution of iron was much less complete and slower than that of manganese. With the first two extractions of 15 min each, only 2 or 3% of the total iron was removed except that sample 429 released 6% of its iron. With eight successive extractions of a total equilibration time of 5 hours, 20% of the total iron was removed from sample 429 but only 6 to 7% from three other samples.

The effect of concentration of the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (in 0.1M HNO_3) and time of shaking on the dissolution of manganese and iron from two sediment samples is shown in Fig. 2 and 3. There was a slight but noticeable effect of both factors on the dissolution of manganese at

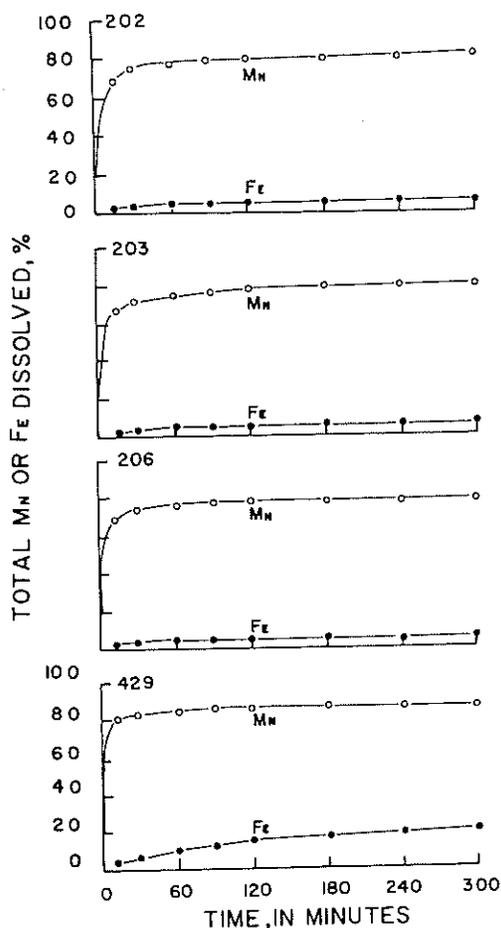


Fig. 1—Accumulative dissolution of manganese and iron from four sediment samples by eight successive extractions with acidified hydroxylamine hydrochloride ($0.1M$ $NH_2OH \cdot HCl$ in $0.1M$ HNO_3) after shaking time of 15, 15, 30, 30, 30, 60, 60, and 60 min.

lower concentrations of the $NH_2OH \cdot HCl$ solution and shorter duration of shaking (Fig. 2). After 60 min of shaking, no significant difference in manganese release was observed, regardless of the concentration of the $NH_2OH \cdot HCl$ solution varying from 0.025 to $.025M$. On the other hand, with 0.1 or $0.25M$ $NH_2OH \cdot HCl$ solution, varying the time of shaking had less effect.

The dissolution of iron was influenced by various concentrations of the $NH_2OH \cdot HCl$ solution and by time of shaking (Fig. 3). The amounts of iron dissolved increased steadily with greater concentrations of the $NH_2OH \cdot HCl$ solution and longer periods of shaking. Here, too, the iron in sample 429 is more soluble in the $NH_2OH \cdot HCl$ solution than the iron in sample 202.

The pH of the $NH_2OH \cdot HCl$ solution was the next factor considered. Its effect after equilibration for 30 min is shown in Table 1. The dissolution of manganese by 0.1 $NH_2OH \cdot HCl$ at pH 3, 2, and 1 was rather constant, amounting to 70 to 80% of the total manganese present in various samples. More iron was dissolved with decrease in pH (increasing acidity) of the $NH_2OH \cdot HCl$ solution; especially so when pH was decreased from 2 to 1. The amount of iron dissolved was 1 to 4% of the total iron

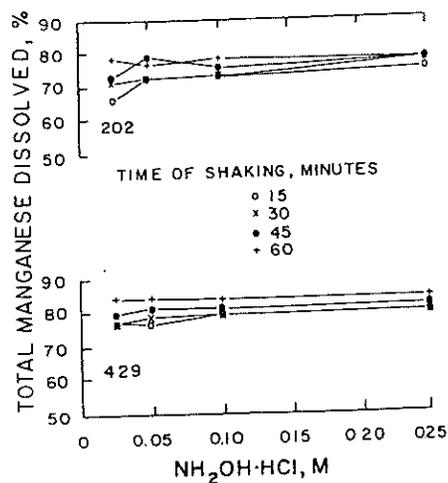


Fig. 2—Effect of concentration of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$ in 0.025, 0.05, 0.1, and $0.25M$ in $0.1M$ HNO_3) and time of shaking (15, 30, 45, and 60 min) on the dissolution of manganese from two sediment samples.

present, except for sample 409A which released 9.4% of its total iron to the $NH_2OH \cdot HCl$ solution at pH 1. Sample 409A was different from other samples in containing considerably greater amounts of both iron and manganese.

On a weight basis, these sediment samples contained more than ten times as much iron as manganese. Nevertheless, manganese was preferentially dissolved by the $NH_2OH \cdot HCl$ solution.

Selective Dissolution of Manganese Oxides from Mineral, Sediment, and Soil Samples

To determine whether the difference in dissolution between manganese and iron observed in sediment samples could be substantiated, the method of extraction with the $NH_2OH \cdot HCl$ solution was tried on six manganese oxides and seven iron oxides, either purchased from commercial sources or prepared in the laboratory. Manganese and iron oxides were equilibrated with $0.1M$ $NH_2OH \cdot HCl$ in $0.1M$ HNO_3 for 60 min. Three synthetic poorly crystallized manganese oxides (α , δ , and γ forms) dissolved instantly. A reagent MnO_2 , which is the β form of manganese dioxide, dissolved in 30 min. Pyrolusite and bog Mn-oxide required 30 to 60 min for complete dissolution. Apparently, the rate of dissolution of manganese oxides is determined, among other factors, by the mineralogical structure. The rapid dissolution of soil or sediment manganese by the $NH_2OH \cdot HCl$ solution indicates the presence of manganese in certain reactive oxide forms. Hematite, goethite, and magnetite dissolved in the $NH_2OH \cdot HCl$ solution very sparingly (a fraction of 1%), whereas, amorphous $Fe(OH)_3$ dissolved to the extent of 8% of its total iron. Presumably, iron oxides in sediment samples (Table 1 and Fig. 3) are in some forms which are intermediate between crystalline iron oxides and amorphous $Fe(OH)_3$ so far as dissolution by the $NH_2OH \cdot HCl$ solution is concerned.

Table 2 presents data on the dissolution of manganese and iron from sediment and soil samples by extraction with $0.1M$ $NH_2OH \cdot HCl$ in $0.01M$ HNO_3 (pH 2). These sam-

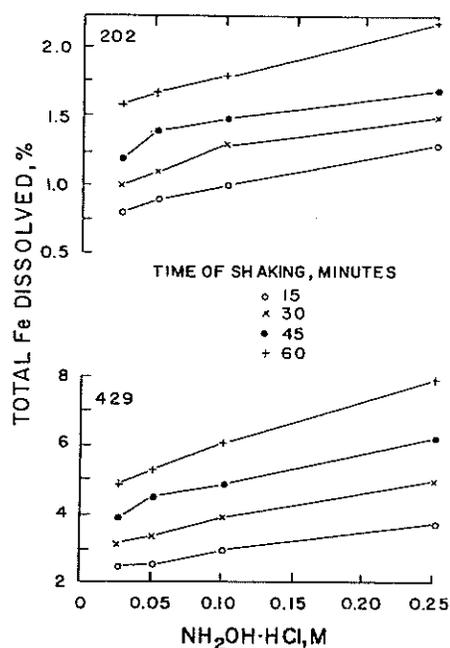


Fig. 3—Effect of concentration of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.025, 0.05, 0.1, and 0.25M in 0.1M HNO_3) and time of shaking (15, 30, 45, and 60 min) on the dissolution of iron from two sediment samples.

ples varied widely in total manganese and iron contents. Of the 10 sediment samples, the amount of total manganese dissolved ranged from 40 (only one sample) to 100% with an average of 85%. Time of shaking seemed less significant after 30 min as observed previously. Manganese in sample 9 (a ferromanganese nodule) and sample 10 (manganese oxide coatings) was extracted effectively by the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution. On the average, only about 5% of the total iron in these 10 samples was removed by extraction. In sample 7, an exception, 17% of its total iron was dissolved; some of the iron may exist as amorphous materials more readily dissolved by the solution.

Four soil samples were taken from the Hawaiian Islands and belonged to the low humid latosol group. Owing to prolonged soil weathering under favorable climatic conditions, both manganese and iron in the soil samples were less extractable by the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution than in the sediment samples. Half of the total manganese and a fraction of 1% of the total iron in the samples were dissolved.

CONCLUDING REMARKS

The solubility of manganese minerals of soils and sediments in the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution is related to several parameters of the mineral species, which may vary as a result of duration of weathering. Among these are mineralogical forms, degree of crystallinity, and particle size or surface area. It is expected that various manganese compounds would respond differently to the action of the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution. By sequential extraction, the rate of dissolution of manganese may reflect the reactivity of the various forms of manganese compounds. Since the major function of the acidified $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution is both reduction and dissolution, the more readily soluble

Table 1—Dissolution of manganese and iron from sediment samples by 0.1M hydroxylamine hydrochloride at pH 3, 2, and 1 (corresponding to 0.001, 0.01, and 0.1M HNO_3 , respectively). Time of shaking: 30 min

Sediment*	Total			Dissolution of sediment			
	Mn %	Fe %	pH	Mn %	Mn % of total	Fe %	Fe % of total
201A	0.28	5.05	3	0.19	67.9	0.042	0.8
			2	0.19	67.9	0.052	1.0
			1	0.20	71.4	0.075	1.5
202	0.45	5.54	3	0.34	75.6	0.043	0.8
			2	0.34	75.6	0.064	1.4
			1	0.36	80.0	0.082	1.6
203	0.46	5.59	3	0.29	63.0	0.049	0.9
			2	0.29	63.0	0.072	1.3
			1	0.31	67.4	0.11	2.0
206	0.46	5.46	3	0.32	69.6	0.064	1.2
			2	0.32	69.6	0.072	1.3
			1	0.33	71.7	0.11	2.0
409A	4.36	27.95	3	3.83	87.8	0.18	0.6
			2	3.62	83.0	0.27	1.0
			1	3.69	84.6	2.62	9.4
429	0.63	5.10	3	0.48	76.2	0.061	1.2
			2	0.50	79.4	0.12	2.4
			1	0.52	82.5	0.21	4.1

* Samples 201A, 202, 203, and 206 were collected in 1969 near Montezuma, Colorado along a stream draining the Cashier mine. Samples 409A and 429 were taken from the San Juan silver mining area, southwest Colorado.

Table 2—Dissolution of manganese and iron from sediments and soils by extraction with acidified hydroxylamine hydrochloride (0.1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.01M HNO_3). Time of shaking: 15, 30 and 60 min

Sample* no.	Total†	Manganese			Iron			
		Extraction of total			Extraction of total			
		15 min	30 min	60 min	Total†	15 min	30 min	60 min
Sediments								
1	0.42	94.3	100.6	101.7	5.48	2.9	3.5	3.8
2	0.11	41.4	42.7	44.1	4.32	1.3	1.6	1.9
3	0.32	65.3	67.7	68.6	4.46	2.8	3.2	3.0
4	0.33	93.0	98.5	97.1	1.54	5.0	5.7	6.7
5	1.22	74.6	80.8	80.6	6.71	2.1	2.2	2.6
6	4.21	83.5	86.9	85.1	6.72	2.5	2.9	4.1
7	9.44	95.7	98.5	100.1	6.10	13.7	17.8	18.8
8	8.39	90.4	93.7	95.7	12.29	5.3	5.3	5.4
9	14.78	97.1	97.5	101.4	18.66	3.1	4.0	4.7
10	43.04	84.1	87.0	88.5	9.98	6.8	6.5	7.7
Average	8.23	81.9	85.4	86.3	7.63	4.6	5.3	5.9
Soils								
11	0.54	40.4	41.7	42.4	19.00	0.1	0.1	0.1
12	0.95	57.6	59.7	61.1	12.10	0.3	0.4	0.4
13	0.34	42.6	43.8	44.7	15.90	0.1	0.1	0.1
14	0.64	58.3	59.8	60.3	15.00	0.1	0.2	0.2
Average	0.62	59.7	51.3	52.1	15.70	0.2	0.2	0.2

* Sample 1 was taken from Montezuma, Colorado; samples 2, 3, 5 and 7 from Washington County, samples 4 and 6 from Hancock County, and samples 8, 9 and 10 from Somerset County, Maine; samples 11, 12, 13, and 14 from sugarcane fields in Hawaii, belonging to the low humid latosol group.

† Determined by sodium carbonate-borax fusion and atomic absorption spectrophotometry. See Methods.

fraction would represent the more reactive secondary manganese oxides which also presumably possess a stronger scavenging action on heavy metal ions.

The difference in solubility of manganese oxides vs. iron oxides in the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution is the basis for a method of separating the two closely related groups of oxides. The concentration and acidity of the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution, as well as the time of equilibration, should be kept low enough to limit the dissolution of iron oxides, but should be sufficient to dissolve manganese oxides effectively. Since this method of extraction is designed mainly for the dissolution of manganese oxides and the associated heavy metal ions, the pH of the $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution should be compatible with the reaction of metal ions in solution. Accordingly, a 0.1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution prepared in 0.01M HNO_3 (pH 2) and a shaking time of 30

min are recommended for the extraction of manganese oxides from soils or sediments. Thereby, most heavy metal ions released along with the dissolution of manganese oxides are prevented from hydrolysis to form insoluble hydroxides or basic salts, and can be determined in solution by appropriate analytical methods. On the average, 85% of the total manganese and about 5% of the total iron from various sediments are dissolved by the recommended method. Dissolution of the total manganese and the total iron from four highly weathered soils amounts to 50% and less than 1%, respectively.

This simple and rapid method of extraction may be advantageously applied to the analysis of drainage sediment for geochemical exploration. Heavy metal ions, released simultaneously with manganese, can be attributed to the scavenging action of manganese oxides. The residue after the dissolution of manganese may be treated for the dissolution of iron oxides. Metal ions associated with iron oxides can then be determined. By dissolving manganese oxides and iron oxides separately and determining metal ions associated with each group of oxides, the geochemical significance of interelement relationships may be established.

Fresh-water and marine ferromanganese nodules are noted for their high content of trace metals (10, 20). Association between trace metals and manganese vs. iron may be determined more accurately by the suggested method than by the bulk analysis, and more conveniently and easily ascertained than by the electron microprobe procedure (5, 13). This method may also be useful in studies related to water pollution caused by excess amounts of heavy metals, since some of the metals in polluted waters are to be scavenged by manganese oxides present in bottom-sediment and/or suspended materials.

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LITERATURE CITED

- Anderson, B. J., and E. A. Jenne. 1970. Free-iron and manganese oxide content of reference clays. *Soil Sci.* 109: 163-169.
- Biswas, T. D., and S. P. Gawande. 1964. Relation of manganese in genesis of catenary soils. *Indian Soc. Soil Sci.* 12:261-267.
- Burns, R. G., and D. W. Fuerstenau. 1966. Electron-probe determination of inter-element relationships in manganese nodules. *Amer. Mineralogist* 51:895-902.
- Canney, F. C. 1966. Hydrous manganese-iron oxide scavenging: its effect on stream sediment surveys (abs.). *Canada Geol. Survey Paper* 66-54:11-12.
- Canney, F. C., and G. A. Nowlan. 1964. Solvent effect of hydroxylamine hydrochloride in the citrate-soluble heavy metals test. *Econ. Geol.* 59:721-722.
- Chester, R., and M. J. Hughes. 1967. A chemical technique for the separation of ferro-manganese minerals, carbonate minerals, and adsorbed trace elements for pelagic sediments. *Chem. Geol.* 2:249-262.
- Daniels, R. B., J. F. Brasfield, and F. F. Riecken. 1962. Distribution of sodium hydrosulfite extractable manganese in some Iowa soil profiles. *Soil Sci. Soc. Amer. Proc.* 26: 75-78.
- Dion, H. G., P. J. G. Mann, and S. G. Heintze. 1947. The "easily reducible" manganese of soils. *J. Agr. Sci.* 37:17-22.
- Harriss, R. C., and A. G. Troup. 1969. Freshwater ferromanganese concretions: chemistry and internal structure. *Science* 166:604-606.
- Harris, R. C., and A. G. Troup. 1970. Chemistry and origin of freshwater ferromanganese concretions. *Limnol. Oceanog.* 15:702-712.
- Hawkes, H. E., and J. S. Webb. 1962. Geochemistry in mineral exploration. Harper and Row, New York and Evanston, 415 p.
- Healy, T. W., A. P. Herring, and D. W. Fuerstenau. 1966. The effect of crystal structure on the surface properties of a series of manganese dioxides. *J. Colloid Interface Sci.* 21:435-444.
- Horsnail, R. F., I. Nichol, and J. S. Webb. 1969. Influence of variations in secondary environment on the metal content of drainage sediments. *Colorado Scho. Mines. Quart.* 64:307-322.
- Jenne, E. A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *In* R. F. Gould (ed.) Trace inorganics in waters. *Advan. Chem. Series* 73:337-389.
- Krauskopf, K. B. 1956. Factors controlling the concentrations of thirteen rare metals in sea-water. *Geochim. Cosmochim. Acta* 9:1-32B.
- Krauskopf, K. B. 1957. Separation of manganese from iron in sedimentary processes. *Geochim. Cosmochim. Acta* 12: 61-84.
- Le Riche, H. H., and A. H. Weir. 1963. A method of studying trace elements in soil fractions. *J. Soil Sci.* 14: 225-235.
- Lynn, D. C., and E. Bonatti. 1965. Mobility of manganese in diagenesis of deep-sea sediments. *Marine Geol.* 3:457-474.
- McKenzie, R. M. 1970. The reaction of cobalt with manganese dioxide minerals. *Aust. J. Soil Res.* 8:97-106.
- Mero, J. L. 1962. Ocean-floor manganese nodules. *Econ. Geol.* 57:747-767.
- Mitchell, R. L. 1964. Trace elements in soils. p. 320-368. *In* F. E. Bear (ed.) *Chemistry of the soil* (2nd ed.), Amer. Chem. Soc. Monograph series. Reinhold Publishing Corp., New York.
- Murata, K. J. 1939. Exchangeable manganese in river and ocean muds. *Amer. J. Sci.* 237:725-735.
- Murray, D. J., T. W. Healy, and D. W. Fuerstenau. 1968. The adsorption of aqueous metal on colloidal hydrous manganese oxide. *In* R. F. Gould (ed.) *Adsorption from aqueous solution*. *Advan. Chem. Series* 79:74-81.
- Nicholson, C. M. 1941. Short volumetric method for the determination of iron in silicates. *Bull. Amer. Ceramic Soc.* 20:331-334.
- Page, E. R. 1964. The extractable manganese of soil. *J. Soil Sci.* 15:93-102.
- Parks, G. A., and P. L. de Bruyn. 1962. The zero point of charge of oxides. *J. Phys. Chem.* 66:967-973.
- Posselt, H. S., F. J. Anderson, and W. J. Weber, Jr. 1968. Cation sorption on colloidal hydrous manganese dioxide. *Environ. Sci. Tech.* 2:1087-1093.
- Robinson, W. O. 1929. Detection and significance of manganese dioxide in the soil. *Soil Sci.* 27:335-350.
- Taylor, R. M. 1968. The association of manganese and cobalt in soils—further observations. *J. Soil Sci.* 19:77-80.
- Taylor, R. M., and R. M. McKenzie. 1966. The association of trace elements with manganese minerals in Australian soils. *Aust. J. Soil Res.* 4:29-39.
- Taylor, P. M., R. M. McKenzie, and K. Norrish. 1964. The mineralogy and chemistry of manganese in some Australian soils. *Aust. J. Soil Res.* 2:235-248.
- Turner, R. R., and R. C. Harriss. 1970. The distribution of non-detrital iron and manganese in two cores from the Kara Sea. *Deep-Sea Res.* 17:633-636.
- White, R. P. 1969. Hydroxylamine hydrochloride as a reducing agent for atomic absorption determinations of manganese in dry-ashed plant tissue. *Soil Sci. Soc. Amer. Proc.* 33:478-479.