

NOTAS CIENTÍFICAS

A FIELD TEST FOR FERROUS IRON AND FERRIC-ORGANIC COMPLEXES IN CERRADOS SOILS¹

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ABSTRACT - A 0.1 M solution of barium chloride containing 1,10-phenanthroline indicator gave a satisfactory field test for exchangeable and water-soluble ferrous iron in Cerrados soils. A 1 ml subsample of soil is added to a vial containing 5 ml of the solution and shaken for 20 seconds. An orange-red colour indicates the presence of ferrous iron. The presence of ferric-organic complexes in soils can also be detected, as the reduction of ferric to ferrous iron in the presence of oxidisable organic ligands is a photochemical process. Subsamples of soils are added to two separate vials containing the solution and shaken for 20 seconds. One vial is kept in the dark and the other exposed to sunlight. After five to fifteen minutes, the development of an orange-red colour in the vial exposed to light in contrast with no colour change in the other, indicates the presence of ferric-organic complexes.

TESTES DE CAMPO PARA FERRO FERROSO E COMPLEXOS FÉRRICO-ORGÂNICOS EM SOLOS DE CERRADO

RESUMO - Uma solução 0,1 molar de cloreto de bário, contendo o indicador 1,10 - fenantrolina, pode ser utilizado como um teste satisfatório feito no campo para detectar a presença de ferro ferroso trocável e solúvel em água nos solos de Cerrados. Este teste consta da adição de 5 ml da solução de cloreto de bário + 1,10 - fenantrolina a 1 ml de solo com agitação por 20 segundos. O desenvolvimento da cor laranja-avermelhado indica a presença de ferro ferroso. A presença de complexos férrico-orgânicos pode também ser detectada, pela redução do ferro férrico a ferroso na presença de ligantes orgânicos oxidáveis por um processo fotoquímico. Subamostras de solos são adicionadas em dois frascos distintos, contendo a solução de cloreto de bário + 1,10 - fenantrolina e agitados por 20 segundos. Um frasco é guardado no escuro e o outro é exposto à luz solar. Dentro de cinco a quinze minutos uma cor laranja-avermelhado é desenvolvida no frasco exposto à luz, enquanto no frasco que permaneceu no escuro não há mudança de cor, o que indica a presença de complexos férricos orgânicos.

¹ Accepted for publication on February 18, 1986.

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In many soils, oxidizing conditions are associated with the red-brown colours of insoluble ferric forms of iron, particularly ferric oxides and hydrous oxides. These contrast with the grey colours common under water-logged conditions, resulting from the reduction of ferric iron to soluble ferrous ions. However, in certain Cerrados (savanna) soils, especially members classified within the broad Latossolo Vermelho Amarelo group of the Brazilian Classification System (Empresa Brasileira de Pesquisa Agropecuária 1981), wet season water-logging occurs without clear colour differentiation.

Recently, Childs (1981) published a new field test for the identification of ferrous iron and ferric organic complexes in New Zealand soils. His test uses a 1 M ammonium acetate extracting solution buffered to pH 7, and contains α , - α' -dipyridyl to indicate the presence of ferrous iron. He avoids the potential problem of the photochemical reduction of ferric to ferrous iron in the presence of organic ligands as reported by Lee & Stumm (1960), McMahon (1967) and Heaney & Davidson (1977), by simply comparing the colour development of two soil subsamples, one kept in the dark and the other left in light. Colour development confined to the subsample left in the light indicates photochemical reduction. Childs notes that this reduction proceeds more rapidly below pH3 compared with rates when pH values are closer to neutral (Theis & Singer 1973), and justifies the use of ammonium acetate solution buffered at pH7 for extracting ferrous ions accordingly. However, doubts may be expressed as to the advisability of using a buffered neutral solution with the predominantly variably charged soils with pH dependence in the Cerrados (Cochrane et al. 1985). In this context, the test using potassium chloride as an extractant described by Richardson & Hole (1979) in their study of mottling and iron distribution in a Glossoboralf-Haplaluquoll hydrosesquence, would be preferable; nevertheless these workers failed to take the possible photochemical reduction of ferric iron to account. It might also be noted that the test for HCl-extractable ferrous iron developed by Hoffer (1945) and described by Jackson (1958) based on the blue colour of the ferrous ferricyanide complex, raises the question of the origin of HCl-extractable iron. The low pH would favour reduction of ferric iron in the presence of organic matter and light.

As no field test suitable for the identification of ferrous iron in Cerrados soils has been reported in the literature, the following was developed: One ml soil subsamples are added to two vials each containing 5 ml of 0.1 M barium chloride solution with 1,10 - phenanthroline indicator at a concentration of 0.2 g/l, and shaken for 20 seconds. One vial is exposed to sunlight and the other kept in the dark to avoid the possible photoreduction of ferric to ferrous iron in the presence of organic ligands. The soil is allowed to settle and the vials inspected at one, five, ten and fifteen minute intervals. An orange-brown colour developed only in the vial exposed to light indicates the presence of light sensitive ferric organic complexes. Colour development in both vials indicates the presence of ferrous iron.

The sensitivity of the test using dilute concentrations of ferrous iron as sulphate may be summarized:

Concentration of Fe ²⁺ , mmol/l	Colour development
0.00179	weak orange pink
0.00895	distinct orange pink
0.01791	distinct orange red
0.08953	strong orange red

The colour development was distinctive in concentrations as low as 0.00895 mmol/l. The colour developed with 1,10 - phenanthroline is stable for several hours. The latter was used in the test as it was available locally and is often used for the quantitative analysis of ferrous iron (Vydra & Kapanica 1963). However, other

indicators including α , α' -dipyridyl (Heaney & Davidson 1977) or bathophenanthroline (McMahon 1969) might be used. The 0.1 M barium chloride solution chosen for the extractant, follows the approach of Gillman (1979), and enables identification of ferrous iron at pH levels approaching those of the soil. However, other neutral salt solutions including potassium chloride could be used. The technique of exposing one vial to sunlight and keeping the other in the dark to identify any photochemical reduction of ferric to ferrous iron, follows from the work of Childs (1981).

The test was subsequently carried out on three distinct soils from sites along a cross-section of the Cerrados landscape at the EMBRAPA-Centro de Pesquisa Agropecuária dos Cerrados, experimental station. These included an upland, poorly drained Latossolo Vermelho-Amarelo (LVA) sited near the edge of a "chapada" (upper plain surface), a well drained Latossolo Vermelho-Escuro (LVE) in an intermediate slope position and a poorly drained hydromorphic found in the lower part of the landscape. None of the soils tested had only light sensitive ferric organic complexes. No Fe^{2+} was identified in the poorly drained LVA upland "chapada" soil even at a depth of 120 cm where it had been saturated with water for about three months. This would indicate that the soil water is well oxygenated due to its lateral movement through the soil. A negative test was given for the LVE soil; this was expected as these are well drained adequately aerated soils. On the other hand, the hydromorphic soil in the lower part of the landscape gave a very strong test for ferrous iron, even at a depth of only 5 cm. It was noted, however, that the strength of this latter test diminished rapidly in soil samples taken back to the laboratory and allowed to dry out. Oxidation on drying follows a predictable pattern, and illustrates the need for examining ferrous iron conditions in the field.

The test identifies water soluble and exchangeable ferrous iron at a pH approximating that of the soil, and takes the possible photochemical reduction of ferric to ferrous iron in the presence of organic ligands to account. It is simple and could readily be used by agronomists to identify potentially iron toxic conditions in poorly drained soils, including "várzeas" being considered for the cultivation of wet-land rice. Further, it would be a useful part of the field kit of soil scientists to help with the study of the dynamics of iron movements both within the soil profile and throughout the landscape.

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