

The routine determination of manganese with formaldoxime

J. CH. VAN SCHOUWENBURG

State Agricultural University, Laboratory of Soils and Fertilizers, Wageningen, and
Institute for Soil Fertility, Groningen, Netherlands

Summary

The interference of iron when manganese is determined using formaldoxime can be successfully masked with KCN in combination with measuring at a wavelength of 500 nm.

1. Introduction

The determination of Mn with formaldoxime is influenced by Fe, Cu, Ni, Co, Ce and V (MARCZENKO, 1964). In plant material or soil extracts the latter three elements do not occur to an extent that might cause serious interference. Cu, Ni and Co can readily be masked with KCN. However, in the alkaline medium necessary for the development of the Mn-formaldoxime colour, KCN and every other masking agent tested by this author, produces a yellow-brown colour with Fe, probably due to the formation of FeOH complexes. These coloured complexes, if present at rather high levels, will in their turn interfere with the determination of Mn.

2. Experimental

VAN DEN HENDE and COTTENIE (1960) describe a method using KCN as a masking agent. In this method formaldoxime is added last, which is rather an attractive feature because in doing so the autooxidation of the reagent is prevented to a large extent, provided the formaldoxime is mixed immediately with the sample to which the other reagents already have been added.

A scaled-down modification of this method was used to study the interference of iron. To solutions containing 25 γ of Mn were added 0, 250, 500 or 1000 γ of Fe. Next, the formaldoxime-Mn colour was developed, the final volume being 25 ml. Spectrograms of the resulting solutions were made. These are presented in FIG. 1.

The spectrograms proved that the influence of iron could be minimized if measurements were made at 500 nm. instead of the 450 nm. normally used.

For the quantitative determination of the interference of iron measurements were made at 450, 500, 520 and 530 nm. For this purpose increasing quantities of Fe were added to solutions containing 20 γ of Mn; the Mn-formaldoxime colour was developed and the final volume made up to 25 ml. The results are presented in the TABLE and in FIG. 2.

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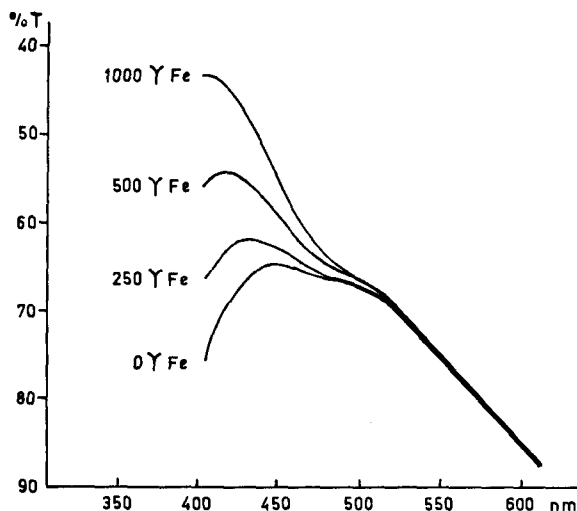


FIG. 1
The influence of increasing quantities of iron on the determination of Mn with formal-doxime

3. Discussion

The iron salt originally used for the experiments, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{ aq}$, contained some Mn as a contaminant. The Fe was therefore extracted from a 6 n HCl medium with ether and back-extracted into 1.2 n HCl.

The results as presented in the TABLE and in FIG. 2 suggest a linear relationship between extinction values and amounts of Fe present.

Furthermore, measurement at a wavelength of 500 nm. resulted in very small interference if Fe with only 9% loss in sensitivity.

If measured at 500 nm. a Fe/Mn ratio of 50 will result in a positive error of about 0.010–0.013 extinction units corresponding with an average relative error of about 8.4%.

In soil and plant analysis such ratios are, according to the author's experience, not to be expected. The Fe/Mn ratio will probably never exceed a value of 20; normally this ratio will be less than 10. Because of the linear character of the interference of Fe, the errors produced with this simplified procedure will probably not exceed

TABLE. Extinction values of solutions containing 20 γ of Mn together with increasing quantities of Fe, measured at different wavelengths

γ of Mn added	γ of Fe added	Extinction values ($\times 1000$) at			
		450	500	520	530 nm
20	0	151	137	126	117
20	250	170	140	129	120
20	500	187	144	131	122
20	750	203	145	133	123
20	1000	219	147	134	124
0	1000	71	13	10	9

Blank values have been subtracted.

4 % and in normal cases be of the order of 2 % or even less. According to FERRARI and VERMEULEN (1955), the variation coefficient of a soil sample will be about 10 % in the case of P, K and Mg. There is no reason to believe that plant samples will show a smaller variation coefficient with these and, probably, other elements. This means that the overall-variation coefficient even in extreme cases, will only increase from 10 % to 10.8 % at a Fe/Mn ratio of 20. If considered necessary, which however seems unpractical, it is possible to correct for the Fe/Mn ratio because the Fe interference proved to be reproducible with the method described.

The measurements were made with an Optica CF4 spectrophotometer. For routine determinations at 500 nm., a colorimeter with interference filters (for instance a Vitatron with 505 filter) can be used as well.

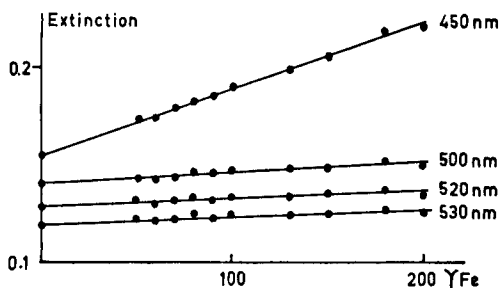


FIG. 2
The influence of the wavelength on the interference of Fe

4. Reagents

Only analytical grade chemicals have been used.

- metol-sulphite solution: dissolve 0.1 g of metol (p-methylaminophenol sulphate), 13.7 g of $\text{Na}_2\text{S}_2\text{O}_5$ and 1 g of $\text{Na}_2\text{SO}_3 \cdot 7 \text{ aq}$ and make up to 100 ml. This solution will keep for at least 1 month.
- alkaline KCN solution: mix 20 ml of KCN 10 %, 100 ml of NH_4OH (s.w. 0.910) and 360 ml of distilled water.
- formaloxime reagent: dissolve 5 g of hydroxylamine-HCl in a mixture of 5 g of formaldehyde 40 % and about 80 ml of distilled water. Make up to 100 ml. This solution will keep for at least 1 month. The procedure of VAN DEN HENDE and COTTENIE is followed here although most authors use less formaldehyde for the preparation of the reagent.
- standard solution of 10 ppm Mn: dissolve in a 600-ml beaker 0.288 g of KMnO_4 in about 200 ml of distilled water to which has been added 45 ml of H_2SO_4 (s.w. 1.84). Reduce the KMnO_4 with a few drops of H_2O_2 30 %. Boil to expel the excess of H_2O_2 . Rinse the cooled solution into a 1-litre volumetric flask and make up to volume. Pipette 100 ml of this solution into a 1-litre volumetric flask and make up to volume.

5. Procedure

The procedure is in fact a scaled-down modification of the procedure of VAN DEN HENDE and COTTENIE.

Pipette into test tubes 2 ml of the sample solution and add 0.5 ml of the metol-

sulphite- and 2.4 ml of the alkaline KCN solution. Mix and wait 15 minutes. Then add 2 drops of the formaldoxime reagent. Mix immediately. Wait 30 minutes before measuring at 500 nm. in a 1-cm cuvette.

The procedure described can also be used with a Morgan's soil extract. For the analysis of plant material it can be applied to all media that, by their acidic nature, do not cause the final pH to drop below a value of 10.

No interferences were found with 100 γ quantities of either Co, Cu, Ni or Zn. Larger quantities have not been tested.

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