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# IMPROVED METHOD OF COLOMETRIC DETERMINATION OF Fe (II) IN THE PRESENCE OF Fe (III) SIGNIFICANCE OF PHOTOREDUCTION PHENOMENA

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For a long time, determination of Fe (II) in the presence of Fe (III) by 1-10-phenanthroline (O-phen) has encountered some difficulties. Many methods were proposed by several authors particularly by VERBEEK (1961) and TAMURA and al. (1974). Their methods seem very interesting but still inadequate. Both methods are based on masking Fe (III) by $NH_4F$ but have different steps in the addition of the reagent.

1. The analytical conditions described by the precedent authors were subject to some changes : the two reagents $NH_4F$ and O-phen are mixed before addition and all manipulations before and during analysis are performed in the dark. By taking such precautions accurate and reliable results can be obtained.

Tests were conducted by using pure solutions of Fe (II), Fe (III) and mixtures of Fe (II) - Fe (III) in mineral (table I) and organic medium (table II).

2. Photoreduction phenomena of Fe (III) in mineral solutions were observed during the conservation of these solutions. In order to check if the same phenomena exist in organic medium, mixtures of Fe (III) - organic acids, were prepared and conserved for various periods of time at light or dark (table III, IV).

Some acids were found to have an intrinsic reduction property that becomes evident just after the mixture of acid - Fe (III) and increases with contact-time ; for other organic acids, it appears only after 24 h contact-time in the dark.

Light induces reduction of Fe (III) whatever the acid. Acid-photolysis causing acid-oxidation often accelerated by ferric salts, leads to this reduction. The magnitude of the photoreduction depends on the nature of the organic acids. Our results, suggest that the photoreduction is usually weak with saturated mono-acids, strong with ethylenic di-acids and even stronger with alcohol acids.

In experimental pedological studies, precautions should be taken concerning light in order to obtain a correct Fe (II)/Fe (III) ratio without Fe (II) overestimation.

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**Table 2 : (Extract) : Determination of Fe (II) by the proposed method in pure solutions of Fe (II) and in mixtures of Fe (II) - Fe (III) in acid medium (mineral and organic). Results are expressed as pg Fe (II) in 10 ml acid.**

| Different acids | Pure solutions of Fe (II) | Fe (II) in pure solutions of Fe (III) | | Fe (II) in the mixtures | |
|---|---|---|---|---|---|
| | 50 µg | 1000 µg | 5000 µg | $M_1$ | $M_2$ |
| HCl | 49,65 | traces | traces | 50 | 49,60 |
| formic | 49,75 | traces | traces | 50 | 49,5 |
| acetic | 49,75 | traces | traces | 50 | 49,75 |
| glycolic | 49,75 | traces | traces | 50 | 49,75 |
| propionic | 50 | traces | traces | 50 | 50 |
| lactic | 50 | traces | traces | 50,25 | 50 |
| pyruvic | 49,5 | 4 | 7,25 | 49,75* | 49,75* |
| succinic | 49,75 | traces | traces | 50 | 50 |
| malic | 49,5 | traces | traces | 50,25 | 50 |
| tartric | 49,5 | traces | traces | 50 | 50 |
| citric | 50 | 0,75 | 1,25 | 49,5* | 49* |
| galacturonic | 49,75 | traces | traces | 50 | 50,25 |
| fulvic | 49 | 14 | 14 | 47,75* | 48,25* |

* After deduction of Fe (II) found in Fe (III)
$M_1$ = 50 µg Fe (II) - 1 000 µg Fe (III) - $M_2$ = 50 µg Fe (II) - 5 000 µg Fe (III).

**Table 4 (Extract) : Influence of contact-time at light or dark of the mixture organic acid - Fe (III) on the final content of Fe (II). Results are expressed as a percentage of Fe (II) in Fe (III).**

| Acids | 0 | dark | | Light | |
|---|---|---|---|---|---|
| | | 24 h | 4,5 days | 24 h | 4,5 days |
| HCl | traces | traces | traces | 2,5 | 4,5 |
| formic | traces | traces | traces | 38,0 | 47,5 |
| acetic | traces | traces | traces | 3,6 | 4,5 |
| glycolic | traces | traces | traces | 26,5 | 25,5 |
| propionic | traces | traces | traces | 1,0 | 2 |
| lactic | traces | traces | traces | 76,5 | 95 |
| pyruvic | 0,5 | 5,5 | 12 | 76,5 | 90 |
| succinic | traces | traces | traces | 5,0 | 6,8 |
| malic | traces | traces | traces | 23 | 17,5 |
| tartric | traces | traces | traces | 62 | 63,0 |
| citric | traces | traces | traces | 85,5 | 100 |
| galacturonic | traces | 8,0 | 12,5 | 31 | 74 |
| fulvic | 5,5 | 20 | 26 | 62 | 65 |


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