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## Iron doping in sodium *para*-nitrophenolate dihydrate crystal: A case study

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### Highlights

- Iron doping in sodium *para*-nitrophenolate dihydrate (**1**) crystal is reexamined.
- Addition of ferric solution into (**1**) results in precipitation of hydrous iron oxide.
- Sharp signals in <sup>1</sup>H NMR spectrum confirm the absence of ferric iron.

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### Graphical Abstract

In view of immediate precipitation of an insoluble brown hydrous iron(III) oxide on addition of ferric solution into aqueous sodium *para*-nitrophenolate dihydrate (**1**), iron cannot be doped in (**1**).



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### *Abstract*

In this study we examine a case of iron doping in sodium *para*-nitrophenolate dihydrate single crystal recently reported by Dalal and Kumar (*Mater. Lett.* 165 (2016) 99-102). We show that, addition of ferric ( $\text{Fe}^{3+}$ ) ions into an aqueous solution of sodium 4-nitrophenolate dihydrate (**1**) results in immediate precipitation of an insoluble brown hydrous iron(III) oxide, which precludes any doping (incorporation) of iron in (**1**). The crystals grown after filtering the precipitate show a negative spot test for iron and exhibit sharp proton resonances in the  $^1\text{H}$  NMR spectrum proving no incorporation of iron in (**1**). In addition to highlighting the importance of the reactive chemistry of the dopant and the host for crystal growth from solution, we show that ferric ions cannot be doped into a host material whose aqueous solution is alkaline.

**Keywords:** Crystal growth; iron doping; sodium *para*-nitrophenolate dihydrate; iron(III) oxide; NMR spectrum

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## 1. Introduction

Doped crystals are an important class of materials and hence the study of their growth, characterization and properties is a current area of research in materials science. Although many claims of growth of doped crystals have appeared in the scientific literature, it has often been observed that the successful incorporation of the dopant has not been proved in many cases for example a claim of iron doping by Dalal and Kumar [1]. As part of our contributions in this area [2-4], we have demonstrated the importance of the compatibility of the crystal structures of the dopant and the host material [2, 3] as well as the reactive chemistry of the dopant with the host [4] for growth of doped crystals.

With a view to address the above matter and highlight the importance of the chemistry of the dopant with the host under the crystal growth conditions, we have chosen 'iron doping' for the present study. In an earlier paper Dalal and Kumar [1] have reported to have doped ferric iron in sodium *para*-nitrophenolate dihydrate (**1**) single crystal by slow evaporation solution growth. Incorporation of Fe<sup>3+</sup> ion as dopant in a Na<sup>+</sup> host crystal can be expected to lead to a charge imbalance and no explanations were offered for overcoming this phenomenon. In addition, there are no reports of any structurally characterised *para*-nitrophenolate compound of iron in the Cambridge Structure Database (CSD) till date [5]. A survey of the literature reveals that (**1**) is a well studied crystalline material [6-11], but there are no reports of doping of any metal ions in (**1**). In view of the above mentioned facts as well as the discovery of a remarkable enhancement in the dielectric, piezoelectric, ferroelectric and SHG properties of sodium *para*-nitrophenolate dihydrate (**1**) due to iron doping by Dalal and Kumar [1], we reexamined the growth of iron doped (**1**) to understand the phenomenon of iron doping. The results of these studies are described in this communication.

## 2. Materials and methods

All the chemicals used in this study were of reagent grade and were used as received without any further purification. Crystal growth studies were performed on a ~2 gram scale of sodium *para*-

nitrophenolate dihydrate (**1**). Pure crystals of (**1**) were prepared by the reaction of *para*-nitrophenol with NaOH in 1:1 mole ratio as per reported methods [7, 8].  $^1\text{H}$  NMR spectra were recorded on a 400 MHz Bruker (Avance) FT NMR spectrometer using  $\text{D}_2\text{O}$  as solvent.

### 3. Experimental

Sodium *para*-nitrophenolate dihydrate (1.97 g,  $10^{-2}$  mol) was dissolved in ~120 ml of double distilled water (solution 1) and the pH of this yellow solution was ~10. In another beaker  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.008 g,  $1.98 \times 10^{-5}$  mol) was dissolved in ~1 ml of double distilled water (solution 2). Solution 2 was added dropwise into solution 1. This immediately resulted in the formation of an insoluble brown precipitate. The precipitate was filtered off and the clear filtrate was allowed to crystallise by slow evaporation method. No special efforts were taken to grow large crystals. The crystalline product (**1-R**) thus obtained was washed well with cold water and air dried (yield = 1.7 g). The label (**1-R**) is given to show that this is the reinvestigated product.

### 4. Results and Discussion

In the present investigation, we studied the crystal growth on a 0.01 mol scale using i) ~2.0 grams of (**1**) and ii) the same dopant viz. ferric nitrate. However, no details of the quantities of reagents employed, the amount of solvent used for crystal growth and the final yield were given for the growth of Fe doped crystal of (**1**) by Dalal and Kumar [4]. In our study, 0.008 g of ferric nitrate nonahydrate amounting to 0.02 mol% of Fe dopant for 0.01 mol of the host crystal was used for crystal growth. We performed the experiment using both water and alcohol as solvent and in both cases same results were obtained. Dropwise addition of an aqueous solution of ferric nitrate into an aqueous solution of pure sodium *para*-nitrophenolate dihydrate resulted in the immediate formation of an insoluble brown precipitate, the amount of which increases with more addition of iron solution (Fig 1). After filtration a clear yellow filtrate, whose colour is same as that of pure crystals of (**1**) in water was obtained. Slow evaporation of the filtrate afforded yellow crystals.

In this context we wish to mention that Dalal and Kumar [1] did not report any precipitate formation. Our results can be correctly explained to the formation of hydrous iron(III) oxide in an alkaline medium, which is a characteristic property of ferric ions in aqueous solution and described in all standard chemistry text books [12]. Dissolution of the brown precipitate in dilute HCl followed by reaction with aqueous ammonium thiocyanate resulted in an intense blood red coloration proving the presence of Fe(III) in the precipitate [13]. The precipitate accounted for all the iron(III) employed in the crystal growth reaction. Thus our study reveals that iron(III) added in the reaction mixture is NOT doped, but completely thrown out from the reaction medium as hydrous iron(III) oxide. Since no iron doping has taken place, there can be no remarkable enhancement in dielectric, piezoelectric, ferroelectric and SHG properties of **1**.

In view of the above mentioned, the crystalline product (**1-R**) grown from the filtrate showed no coloration whatsoever with aqueous thiocyanate solution and gave a negative test. Since, the thiocyanate reaction is a characteristic spot test to detect trace amounts of iron (sensitivity 0.25  $\mu\text{g}$ ) [13] the presence of any trace iron(III) in (**1-R**) can be conveniently ruled out. To further prove the absence of iron, (**1-R**) was investigated by  $^1\text{H}$  NMR spectroscopy. The spectrum exhibits a characteristic AA'BB' pattern for the aromatic protons of the *para*-nitrophenolate moiety (Fig. 2). As it is well known that paramagnetic impurities broaden NMR signals [14, 15], the observed sharp resonances unambiguously prove the absence of any iron(III) in (**1-R**). In accordance with this, the NMR spectrum of (**1-R**) is identical to the spectrum of pure crystals of (**1**). The authors had reported that the IR spectrum of the pure material is same as that of a so called iron doped crystal which can now be correctly explained due to the absence of any iron(III) since (**1**) and (**1-R**) are one and the same material. The non-incorporation of iron(III) in (**1**) is not at all surprising since it is well known that ferric remains in solution only in strongly acidic medium as  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . In contrast, an aqueous solution of (**1**) which is a salt of weak acid and strong base is quite alkaline (pH  $\sim$ 10). Thus the reactive chemistry of iron rules out any doping. Although Dalal and Kumar [1] reported that “*In EDAX analysis the presence of iron in FSPNPD crystal was confirmed, but due to the small amount of iron nitrate, it is difficult to quantify iron in a crystalline matrix*” we opine that an EDAX study is

no confirmatory proof for doping. The improper use of EDAX for characterising doped crystals has been recently highlighted [16]. The EDAX claim of Dalal and Kumar [1] can be better explained due to trace amounts of hydrous iron(III) oxide on the crystal surface and not due to any doping.

Although the title crystal sodium *para*-nitrophenolate dihydrate (**1**) has been the subject of several investigations [6-11], Dalal and Kumar were the first to report a claim of discovery of ferroelectric properties for pure crystals of (**1**) by presenting unsaturated elliptical P-E loop at room temperature [1]. According to Dalal and Kumar Fe doping in (**1**) resulted in a remarkable enhancement of the ferroelectric, piezoelectric and SHG properties. In recent papers [17, 18] it has been shown that the elliptical P-E loops reported by Dalal and Kumar are very typical of dielectric loss and not due to any ferroelectric properties. In addition, Tylczynski [18] had reported that a tenfold enhancement in the value of the piezoelectric coefficient is just impossible due to iron doping and attributed this to measurement error. The present findings which prove no incorporation of iron in **1**, unambiguously confirms that the earlier reported claim of enhancement of ferroelectric, piezoelectric and SHG properties of iron doped sodium 4-nitrophenolate dihydrate is untenable.

### 5. Conclusions

In summary, we prove Fe(III) ions cannot be doped in sodium *para*-nitrophenolate dihydrate single crystal with the aid of simple chemical tests and NMR spectroscopy. The present case study demonstrates the importance of the reactive chemistry of dopant and host for growth of doped crystals from solution and shows that iron doping cannot be performed in crystalline materials whose aqueous solutions are alkaline in nature.

### Acknowledgements

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Fig. 1 Addition of ferric solution results in the formation of brown hydrous iron oxide. For a complete sequence of the crystal growth reaction see Fig. S1.

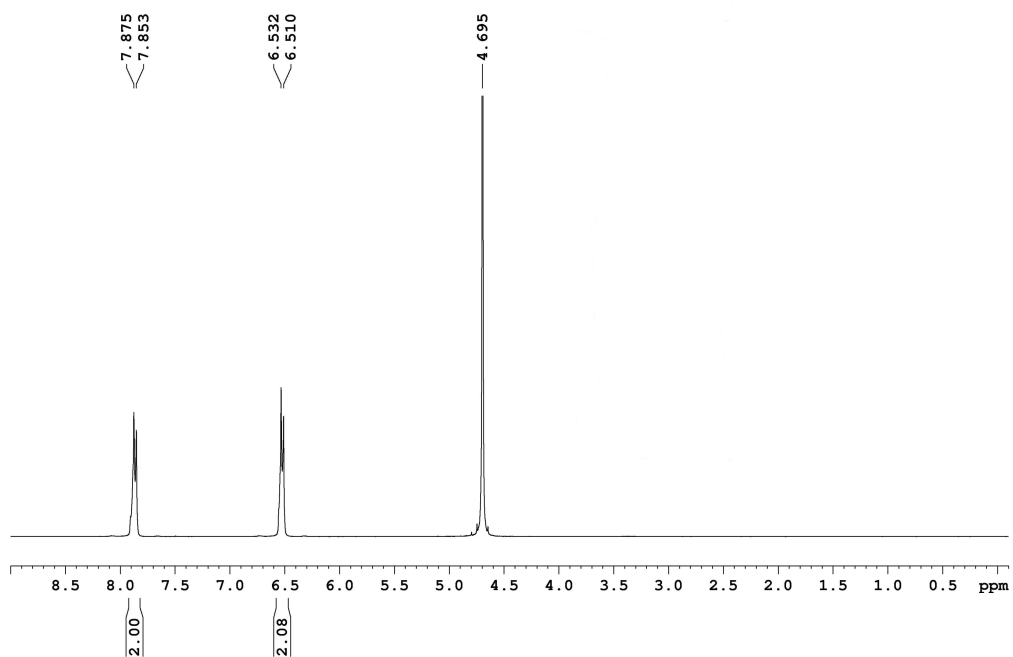


Fig. 2  $^1\text{H}$  NMR spectrum (400 MHz) of **(1-R)** in  $\text{D}_2\text{O}$  showing a typical AA'BB' pattern. For clarity, the resonances of the AA'BB' pattern is expanded and shown as inset. The intense signal at  $\delta = 4.695$  ppm is due to the residual protons of  $\text{D}_2\text{O}$ .

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### **SUPPLEMENTARY MATERIAL ONLINE VERSION**

In the following pages we provide visuals (Fig. S1) of the addition of ferric ions resulting in immediate formation of the insoluble hydrous iron oxide. The formation of brown precipitate is very much in accordance with the chemistry of iron. In support of this chemistry we provide evidence from ref. 12 which is a standard text book.

Filtration of the reaction mixture results in a clear filtrate and the brown precipitate on the filter paper which accounts for all of the iron employed in the crystal growth reaction. experimental chemistry of the crystal growth reaction. The test employed to prove the presence of iron in the precipitate is a very sensitive test. For details Ref. 13 is attached as the last page.

Given below is the sequence of events that occur when ferric ions are introduced into an aqueous solution of sodium *para*-nitrophenolate dehydrate (Fig S1a). Addition of  $\text{Fe}^{+3}$  ions results in immediate precipitation of the hydrous iron oxide the amount of which increases progressively with addition of more  $\text{Fe}^{+3}$ . (Middle row Fig. S1b). After filtration, a clear solution (Fig. S1c) is obtained along with the insoluble matter on the filter paper (Fig. 1d). Slow evaporation results in formation of 1-R described in the experimental.

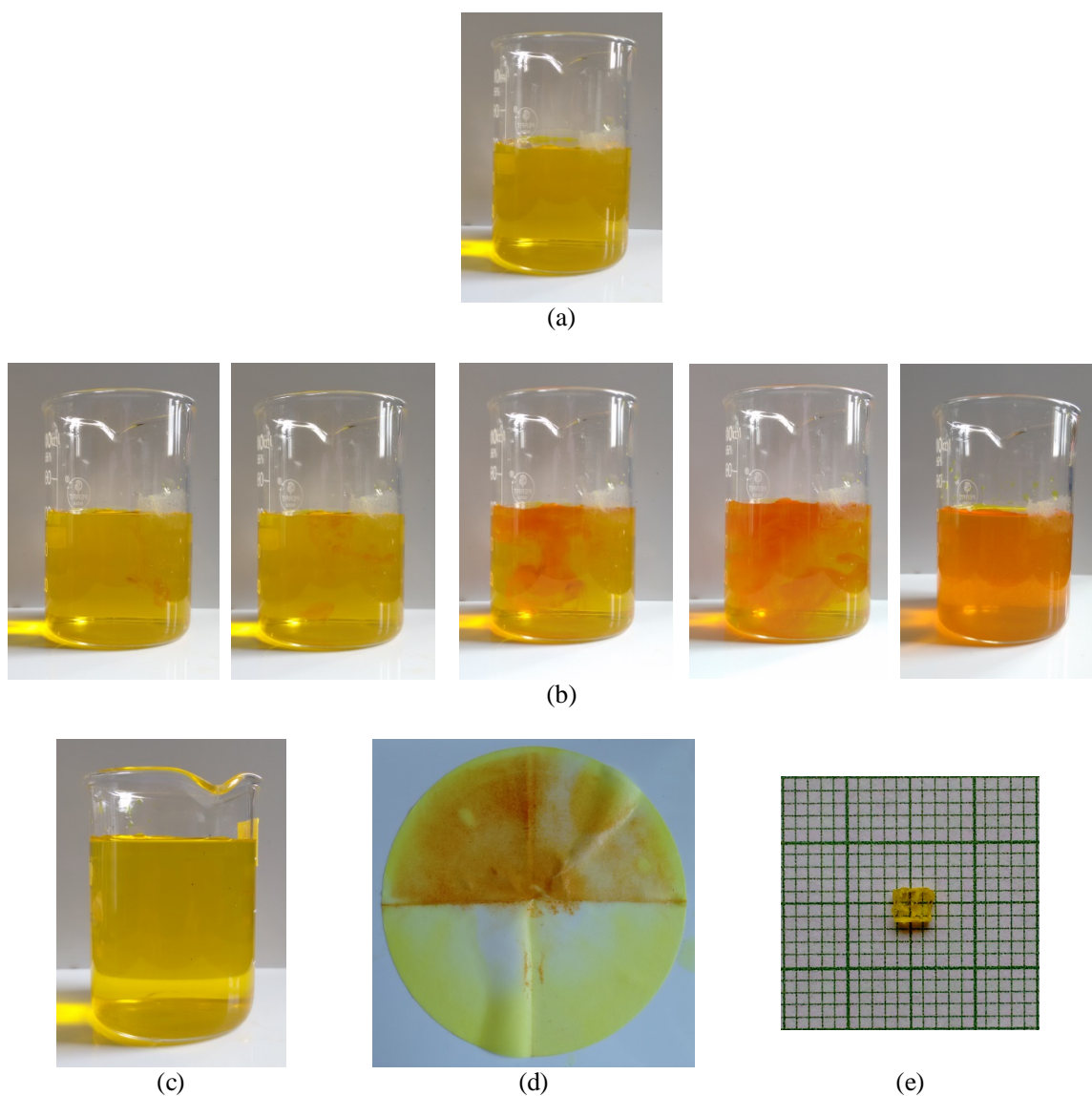


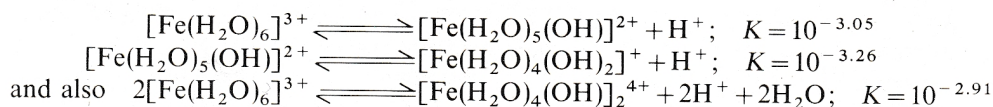
Fig. S1 (a) An aqueous solution of sodium *para*-nitrophenolate dihydrate (solution 1); (b) Dropwise addition of ferric nitrate solution into aqueous sodium 4-nitrophenolate dihydrate results in the formation of brown precipitate; (c) filtrate after removal of brown precipitate; (d) Brown precipitate on the filter paper; (e) **1-R**

## §25.3.4

## Complexes

1265

solutions of salts such as the perchlorate the following equilibria are important:



(The dimer in the third equation is actually<sup>(18)</sup>  $[(\text{H}_2\text{O})_4\text{Fe} \begin{array}{c} \text{OH} \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \text{Fe}(\text{H}_2\text{O})_4]^{4+}$  and

weakly coupled electron spins on the 2 metal ions reduce the magnetic moment per iron below the spin-only value for 5 unpaired electrons.)

It is evident therefore that Fe<sup>III</sup> salts dissolved in water produce highly acidic solutions and the simple, pale-violet, hexaquo ion only predominates if further acid is added to give pH ~0. At somewhat higher values of pH the solution becomes yellow due to the appearance of the above hydrolysed species and if the pH is raised above 2–3, further condensation occurs, colloidal gels begin to form, and eventually a reddish-brown precipitate of **hydrrous iron(III) oxide is formed** (see p. 1254).

The colours of these solutions are of interest. Iron(III) like manganese(II), has a d<sup>5</sup> configuration and its absorption spectrum might therefore be expected to consist similarly (p. 1232) of weak spin-forbidden bands. However, a crucial difference between the ions is that Fe<sup>III</sup> carries an additional positive charge, and its correspondingly greater ability to polarize coordinated ligands produces intense, charge-transfer absorptions at much lower energies than those of Mn<sup>II</sup> compounds. As a result, only the hexaquo ion has the pale colouring associated with spin-forbidden bands in the visible region of the spectrum, while the various hydrolysed species have charge transfer bands, the edges of which tail from the ultraviolet into the visible region producing the yellow colour and obscuring weak d–d bands. Even the hexaquo ion's spectrum is dominated in the near ultraviolet by charge transfer, and a full analysis of the d–d spectrum of this and of other Fe<sup>III</sup> complexes is consequently not possible.

Iron(III) forms a variety of cationic, neutral, and anionic complexes, but an interesting feature of its coordination chemistry is a marked preference (not shown by Cr<sup>III</sup> with which in many other respects it is similar) for *O*-donor as opposed to *N*-donor ligands. Ammines of Fe<sup>III</sup> are unstable and dissociate in water; chelating ligands such as bipy and phen which induce spin-pairing produce more stable complexes, but even these are less stable than their Fe<sup>II</sup> analogues. Thus, whereas deep-red aqueous solutions of  $[\text{Fe}(\text{phen})_3]^{2+}$  are indefinitely stable, the deep-blue solutions of  $[\text{Fe}(\text{phen})_3]^{3+}$  slowly turn khaki-coloured as polymeric hydroxo species form. By contrast, the intense colours produced when phenols or enols are treated with Fe<sup>III</sup>, and which are used as characteristic tests for these organic materials, are due to the formation of Fe–O complexes. Again, the addition of phosphoric acid to yellow, aqueous solutions of FeCl<sub>3</sub>, for instance, decolourizes them because of the formation of phosphato complexes such as  $[\text{Fe}(\text{PO}_4)_3]^{6-}$  and  $[\text{Fe}(\text{HPO}_4)_3]^{3-}$ . The deep-red  $[\text{Fe}(\text{acac})_3]$  and the green  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  are other examples of complexes with oxygen-bonded ligands although the latter, whilst very stable towards dissociation, is photosensitive due to oxidation of the oxalate ion by Fe<sup>III</sup> and so decomposes to Fe(C<sub>2</sub>O<sub>4</sub>) and CO<sub>2</sub>.

<sup>18</sup> T. I. MORRISON, A. H. REIS, G. S. KNAPP, F. Y. FRADIN, H. CHEN, and E. KLIPPERT, Extended X-ray absorption fine structure studies of the hydrolytic polymerization of iron(III). 1. Structural characterization of the  $\mu$ -dihydroxo-octaquoiron(III) dimer, *J. Am. Chem. Soc.* **100**, 3262–4 (1978).

## 3.22 Reactions of the cations

The excess of acetate ions acts again as a buffer and the reaction goes to completion.

Cupferron  
↓  
brown ppt

10. *Cupferron reagent, the ammonium salt of nitrosophenylhydroxylamine, C<sub>6</sub>H<sub>5</sub>N(NO)ONH<sub>4</sub>* reddish-brown precipitate is formed in the presence of hydrochloric acid:



The precipitate is soluble in ether. It is insoluble in acids, but can be decomposed by ammonia or alkali hydroxides, when iron(III) hydroxide precipitate is formed.

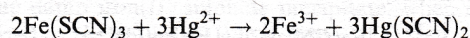
NH<sub>4</sub>SCN  
↓  
red colour

11. *Ammonium thiocyanate solution* in slightly acidic solution a deep-red colouration is produced (difference from iron(II) ions), due to the formation of a non-dissociated iron(III) thiocyanate complex:



Specific for Fe(III)

This neutral molecule can be extracted by ether or amyl alcohol. Fluorides and mercury(II) ions bleach the colour because of the formation of the more stable hexafluoroferrate(III) [FeF<sub>6</sub>]<sup>3-</sup> complex and the non-dissociated mercury(II) thiocyanate species:



The presence of nitrites should be avoided because in acidic solution they form nitrosyl thiocyanate NOSCN which yields a red colour, disappearing on heating.

The reaction can be adapted as a spot test and may be carried out as follows. Place a drop of the test solution on a spot plate and add 1 drop of 0.1M ammonium thiocyanate solution. A deep-red colouration appears.

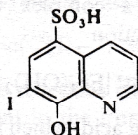
Sensitivity 0.25 μg Fe<sup>3+</sup>

Concentration limit 1 in 200 000.

Coloured salts, e.g. those of copper, chromium, cobalt, and nickel, reduce the sensitivity of the test.

Ferron  
↓  
greenish-blue colour

12. *Ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid) reagent*



green or greenish-blue colouration with iron(III) salts in faintly acid solution (pH 2.5–3.0). Iron(II) does not react: only copper interferes.

Place a few drops of the slightly acid test solution in a micro test-tube and add 1 drop of the reagent. A green colouration appears.

Sensitivity 0.5 μg Fe<sup>3+</sup>.

Concentration limit 1 in 1 000 000.