

## Synthesis and Characterization of Ferrate (VI) Alkali Metal by Wet Method

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**Abstract:** The syntheses of ferrate (VI) appear to be very delicate, this is due to the instability that gives them their high oxidizing power. Although the existence of alkaline ferrate has been cited and testified for a century [1], [2], they have not been a considerable number of studies, because of the instability and difficulties encountered during their preparation.

The wet oxidation passes through the oxidation of a ferric solution to form the solution of ferrate (VI) in strongly alkaline medium. As the solution of ferrate can decompose quickly, protocols of washing and drying precipitation are required to obtain a stable and solid (Ockerman and Schreyer, 1951) [3]; (Schreyer et al, 1953) [4]. The wet method, considered the most practical is still very expensive (Lee et al, 2004) [5]. The phases obtained were characterized by IR X-ray, Spectrometry, Mössbauer spectroscopy, and analysis thermogravimetric.

**Keywords:** Ferrates; bactericidal; oxidant; flocculant, coagulant.

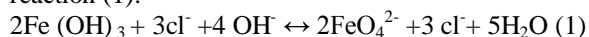
### I. Introduction

Our purpose is to prepare compounds based on iron (VI) stable and track their degradation over time. The preparation phase of  $\text{Na}_2\text{FeO}_4$  was performed by wet method. Their oxidizing power makes it possible to use them as oxidizing and disinfection agent in water treatment. It first reacts in the form of iron (VI) by causing oxidation during which it is reduced to Fe (III). However, the iron (III) is used to treat waste water to precipitate the phosphate.

The induced oxidation is not accompanied by unwanted byproducts.

### II. Synthesis

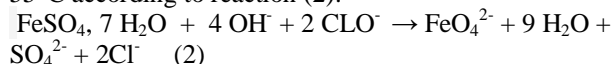
Publications and patents on methods of  $\text{K}_2\text{FeO}_4$  synthesis [6], [7], [8] recommend the use of a ferric salt, which led us to use ferric sulfate derived from an initial oxidation of ferrous sulphate by household bleach. H.HROSTOWSKI and A. SCOTT [9] proposed in 1950 a method of preparation of ferrates, with a purity rate of 97% by oxidation of ferric chloride by sodium hypochlorite in a concentrated solution of sodium hydroxide at a temperature between  $50^\circ\text{C}$  and  $55^\circ\text{C}$ . This synthesis is carried out by applying the following reaction (1):



However, for environments in which were operating H.HROSTOWSKI and Al, in this case in highly concentrated NaOH,  $\text{Na}_2\text{FeO}_4$  is assumed to be very soluble while NaCl has precipitated in the solution [10]. A separation by filtration is then made possible.

### Procedure

Mixing the hydrated iron sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and ClO bleach concentrated in a basic medium. The mixture is stirred for one hour at a temperature between  $50^\circ\text{C}$  and  $55^\circ\text{C}$  according to reaction (2):



$\text{Na}_2\text{FeO}_4$  recovery is done by vacuum filtration. This phase is dried in an oven at  $120^\circ\text{C}$  for 12 hours then placed in a desiccator. During these tests; we find that the yield of the oxidation of ferric sulphate varies with temperature in Figure 1.

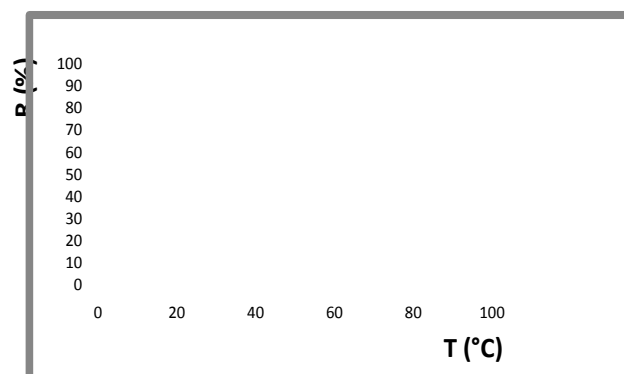


Figure 1. Performance of the oxidation of ferric sulfate as a function of the temperature in concentrated NaOH.

### III. Characterizations

#### 1. Infrared spectrometry

The appearance of an infrared spectrum is related to the symmetry of the molecule or study group for  $\text{FeO}_4^{2-}$  with tetrahedral structure, we expected to find out: First, the fundamental bands characteristic of a symmetry  $T_d$ : either bands  $\nu_3$  and  $\nu_4$  from the two degenerate modes of vibration: the symmetric stretching and angular deformation within the tetrahedron resulting in inactive modes in infrared absorption, bands  $\nu_1$  and  $\nu_2$  must be absent from the spectra [11]. On the other hand, a similarity between the infrared spectra of isomorphous series [12].

The presence of a band  $\nu_1$  and a triplet for  $\nu_3$  (elongation of the tetrahedron) have led w. Griffith [13] to

consider a lower symmetry in  $2d$ , very close to  $2s$  for the  $FeO_4^{2-}$  anion.

IR spectroscopy is a quantitative method for the determination of Iron (VI) in the ferrate compounds. The shape of the spectra is related to the symmetry of the molecule or  $FeO_4^{2-}$  group (tetrahedral structure). The  $Na_2FeO_4$  IR spectrum Figure .2 showed in the field of high frequency an identical appearance to that obtained (mode  $825$  and  $780\text{ cm}^{-1}$ ) P. Tarte and g.nizete [14].

By comparing the outgoing lines  $825\text{ cm}^{-1}, 750\text{ cm}^{-1}$  in the IR spectrum Figure. 2.  $Na_2FeO_4$  phase with that of P. Tarte and G. Nizete [14], we notice that there is a great similarity of these spectra with an isomer shift of  $Na_2FeO_4$  rays that, could be caused by of the preparation and crystallization.

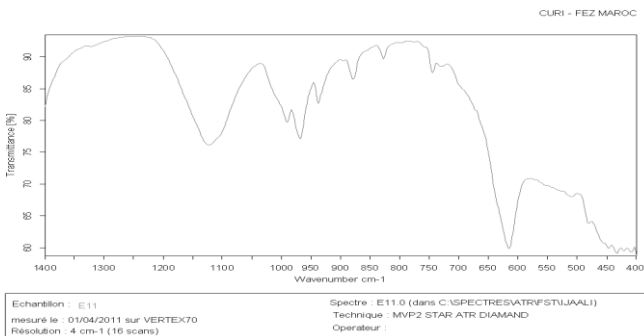
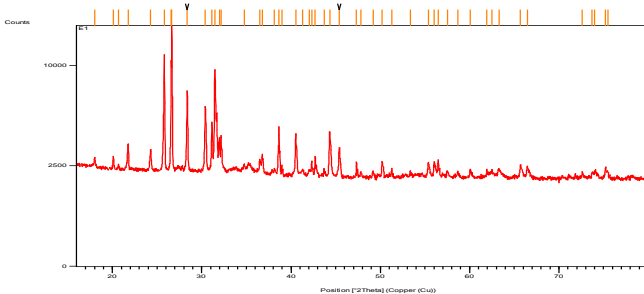


Figure. 2. Spectrometer infra-red  $Na_2FeO_4$ .

**2. X-Ray diffraction**

Measures by a radiation ray diffractometer  $CuK\alpha$  of a compound of  $Na_2FeO_4$  ferrate powder Figure .3 make it possible to verify the crystal structure of ferrate [15], [16], and demonstrate the existence of an isomorphism with  $K_2FeO_4$  and  $BaFeO_4$  as proved by Stuart Licht, Vera. Naschitz and collaborators [17]. The X-ray diffraction is one of the means used to verify the presence of ferrate. The spectrum obtained on  $Na_2FeO_4$  bears a strong similarity with that of isomorphous compounds. There is a splitting of the lines corresponding to planes (102), (202), (013), (200), (020), (112) [18], [19], [20], [21]. The results obtained by infrared support those of XRD.



Figure; 3. Diffractometer XR of  $Na_2FeO_4$

**3. ATG spectrum**

Two decomposition stages were obtained in the TGA curve up to  $500\text{ }^\circ\text{C}$  Figure 4. A first above  $100\text{ }^\circ\text{C}$  corresponding to the

evolution of water weakly adsorbed by the sample and a second step between  $210$  and  $310\text{ }^\circ\text{C}$  corresponding to the release of  $O_2$  Scholder et al [27] and [28].

The two stages of decomposition was accompanied By one endothermique heat effects as measured by DTA.

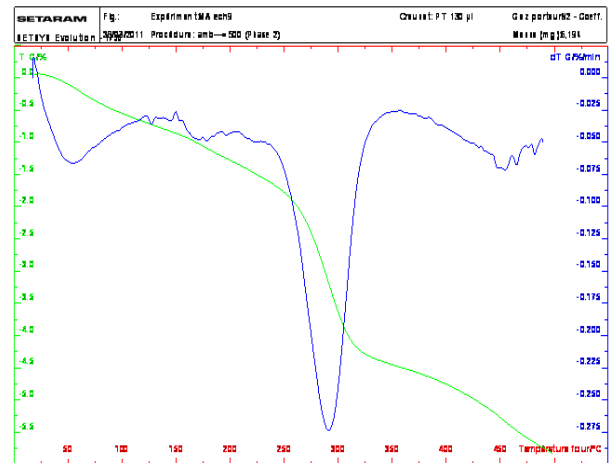


Figure. 4. ATG spectrum of  $Na_2FeO_4$ .

**IV. Tracking ferrate degradation as a Function of time**

**Analysis by Mössbauer spectroscopy**

The Mössbauer effect is obvious benefit to the absorption of a photon  $\gamma$  by a nucleus of  $^{57}Fe$  (present at a rate of about 2.6 percent in the natural iron): we gradually make the energy of the emitted photon vary by the speed of the source ( $^{57}Co$ ). When the latter reaches a value equal to the difference between the energy level of the core in its ground state ( $l = 1/2$ ) and its level in the excited state ( $l = 3/2$ ) the photon is absorbed. This phenomenon translates into a peak on the spectrum Mössbauer spectroscopy also helped to Highlight the existence of magnetic order at low temperature [22], [23], [24], [25], [26].

$Na_2FeO_4$  characterization by Mössbauer spectroscopy after ten months of storage at room temperature reveals a degradation of Iron (VI) with time according to the spectrum in Figure. 5. It is in the form of a enlarged magnetic component calculated by the superposition of two sextuplets and a paramagnetic component adjusted by a paramagnetic doublet. The hyperfine parameters deduced from the calculation are given in chart below.

Table: hyperfine parameters deduced from the calculation of the spectrum after ten months of storage.

$H_{hyp}$  = champ hyperfin, A = poids de la composante en % du spectre total.

	Composante élargie			Composante paramagnétique					
	Sextuplet 1		Sextuplet 2	Doublet					
	$H_{hyp}$ (kOe)	ISO (mm/s)	A (%)	$H_{hyp}$ (kOe)	ISO (mm/s)	A (%)	$\Delta EQ$ (kOe)	ISO (mm/s)	A (%)
$\Sigma$	490	0,22	7,5	449	0,34	1,6	0,512	0,35	90,7

This degradation is manifested spectrum of the isomer shift to 0.22 mm/s for sextuplet 1 and 0.34 mm/s for sextuplet 2 (see table). While the iron sextuplet (VI) comes close to -1. [22], [23], [24], [25], [26]. This isomer shift is due to the degradation of Fe (VI) to iron (III) because of moisture.

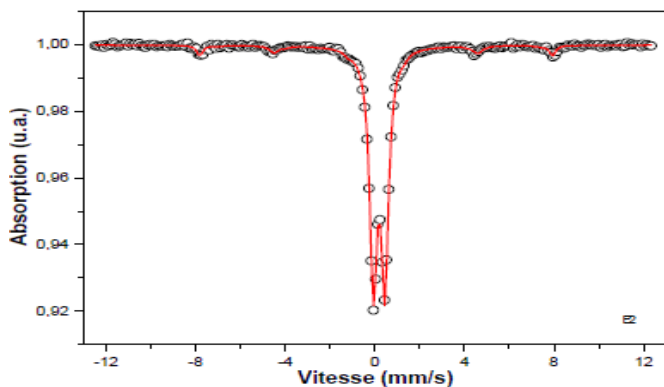


Figure. 5. Mössbauer spectrometer  $\text{Na}_2\text{FeO}_4$  after ten months of storage.

### V. Conclusion

We developed a ferrate (VI) alkaline, ie  $\text{Na}_2\text{FeO}_4$ , by Wet method at a temperature between  $50^\circ\text{C}$  and  $55^\circ\text{C}$ .

The synthesized ferrate present diffractogram similar to those given in the literature.

Infrared spectroscopy shows that we are dealing with a compound containing the  $\text{FeO}_4^{2-}$  group.

Mössbauer spectroscopy of iron allowed us to visualize the oxidation of iron and therefore control the rate of iron (VI), and the monitor of its degradation in iron (III) over time.

The XRD spectrum of  $\text{Na}_2\text{FeO}_4$  is isomorphic to that of  $\text{K}_2\text{FeO}_4$  literature given by the literature. The TGA spectra show a peak at  $100^\circ\text{C}$  corresponding to the departure of water and a peak at  $295^\circ\text{C}$  corresponding to the decomposition of  $\text{Na}_2\text{FeO}_4$ .

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