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KINETIC–THERMOMETRIC METHOD FOR THE DETERMINATION OF Fe(III) IN PETROLEUM PRODUCTS

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ABSTRACT

A new kinetic–thermometric method has been applied to determine Fe(III) in petroleum products. This method is based on the catalytic action of the Fe(III)–TETA (triethylenetetramine) complex on the decomposition of hydrogen peroxide in basic media.

The linear response range is 1.25–13 ng ml^{-1}, with a relative standard deviation of 2.5% for 10 ng ml^{-1} of Fe(III). It is known that a lot of metal ions catalyze this reaction, but no significant interference occurs when this method is applied to petroleum products.

INTRODUCTION

It is known that the decomposition of hydrogen peroxide in basic media is catalyzed by a large variety of substances [1].

A very efficient catalyst for the decomposition of hydrogen peroxide can be made by combining triethylenetetramine (TETA) with ferric ion. One study with Fe(III) has been reported by Wang [2,3].

It is well known that the active complex is $(TETA)Fe(OH)_2^+$. The rate of catalytic decomposition of H_2O_2 was first studied by direct titration [3] and by a manometric method [4].

Several ligands such as ethylenediamine (EDA) and diethylenetriamine (DETA), which form chelate compounds with Fe(III) ion, have been previously studied, but the catalytic efficacy of these chelates to decompose hydrogen peroxide is much lower than that of $(TETA)Fe(OH)_2^+$ [2].

A study of different metal ions has been carried out. Only the TETA chelates of Fe(III) and Mn(II) showed remarkable catalytic activity in the decomposition of H_2O_2. These chelates are $(TETA)Fe(OH)_2^+$ and $(TETA)Mn(OH)^+$ [2].

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Another work [5] indicated the possibility of the determination of the decrease in the concentration of hydrogen peroxide by using biamperometrical and thermometrical techniques The former because of its depolarizing action on the double platinum electrode, and the latter following the heat produced during the decomposition of hydrogen peroxide, as a physical product of the reaction

In previous papers [6–9] we have studied the determination of trace levels of several metal ions employing the kinetic–thermometric technique, with promising results In the present paper we have optimized this reaction in order to determine Fe(III) in petroleum products

The method has been compared with atomic absorption spectroscopy (AAS), a traditional method to analyze Fe(III) in these samples [10,11]

EXPERIMENTAL

Apparatus

The thermometric system has been described elsewhere [6–9], and is composed of an adiabatic nylon cell, a stirrer, a rapid response thermistor of the thermometer type of 100 kΩ at 25 ° C, and a Wheatstone bridge connected to a stabilized voltage source and to a recorder with high input impedance A precision syringe is used to achieve rapid addition of the reagent into the thermometric cell

Atomic absorption measurements were performed in a IL-551 AA spectrophotometer, using the conditions recommended by the manufacturer's manual

Reagents

Standard Fe(III) solution 1000 ppm (Titrisol Merck) Different solutions were prepared from this stock solution by dilution Standard 0 974 M NH_4OH solution was prepared by dilution of concentrated NH_4OH (R A Panreac) Standard 23 87% H_2O_2 (w/v) solution was prepared by dilution of H_2O_2 33% (R A Panreac) A 4 2% solution of TETA was prepared by dilution of concentrated triethylenetetramine (R A Fluka)

Mineralization method

The sample is first treated with concentrated sulphuric acid and the mixture reduced to acid-free coke, and dry ashed at 525 ° C The inorganic ash is dissolved in hydrochloric acid and diluted with water in a volumetric flask to the appropriate final volume [10]

The required sample size depends on the amount of iron present An appropriate amount of sample is weighed into a borosilicate glass beaker, and 1 ml of concentrated H_2SO_4 is added for each gram of sample The size of the beaker should be at least three to four times the combined volume of acid and sample, and no more than 100 g of sample should be treated with acid at one time The beaker is placed on a hot plate in a well-ventilated hood Later, the beaker containing the dry coke is placed into a muffle furnace at 150 ° C, the temperature is increased to 525 ° C, and a slow flow of air is introduced into the furnace to enhance the reduction of the coke to inorganic ash [10]

The inorganic ash is dissolved in hydrochloric acid and diluted with water in a volumetric flask The Fe(III) concentration of this sample is determined both by AAS and kinetic–thermometric techniques More diluted solutions have been obtained according to the initial level of Fe(III) in the sample

Procedure

In order to achieve the best sensitivity, the following procedure is proposed· place 10 ml of 0 974 mol l^{-1} NH_4OH, 5 ml of 4 2% TETA solution, the volume of the required sample (for a 1 25–13 ng ml^{-1} Fe(III) concentration range), and distilled water to a final volume of 80 ml When the baseline becomes horizontal, inject 0 2 ml of H_2O_2 with a precision syringe and register the thermometric curve The initial rate is calculated directly from the slope $\Delta T/t$ of the thermometric curve

RESULTS AND DISCUSSION

Examples of the thermometric curves are shown in Fig 1, where different tg α values are obtained for several Fe(III) concentrations In the operational range, the thermometric curves show good linearity, and the slopes increase with the Fe(III) concentration

Study of the optimum reaction conditions

A number of experimental conditions have to be optimized in this method in order to be quantitatively applicable to the determination of Fe(III) On one hand there has to be a proportional relationship between the reaction rate and the concentration of the catalyst, and on the other hand, the reaction rate in the absence of the catalyst must be insignificant

In order to achieve maximum reagent concentrations with minimum temperature increments of the blanks, we have studied the [NH_4OH], [TETA] and the quantities of H_2O_2 added All these results are shown in Figs 2–4 The concentration of hydrogen peroxide is limited by the injec-

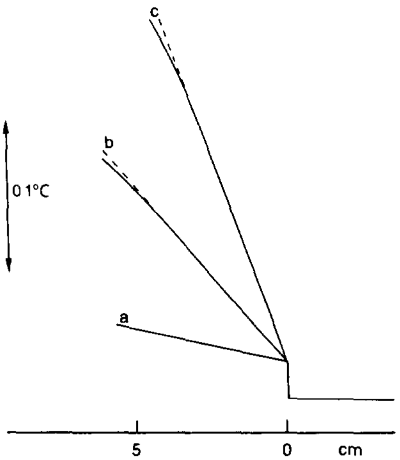

Fig 1 Kinetic-thermometric curves of the H_2O_2-NH_4OH solution, calatyzed by Fe(III)-TETA complex [TETA] = 0 26% $[NH_4OH] = 0\ 112$ mol l^{-1} Addition of 0 2 ml 23 9% H_2O_2 $S = 50$ mV $V_0 = 80$ ml (a), Blank determination, (b), [Fe(III)] = 5 ppb, (c) [Fe(III)] = 12 5 ppb

tion volume, since an increase of injection volume produces a considerable distortion of the thermometric curve

The use of the precision syringe in necessary to obtain good results, since the H_2O_2 concentration is the most important term in the kinetic study A small variation of $[H_2O_2]$ produces a considerable change of tg α value

The best conditions found for the blank are those described in the experimental section

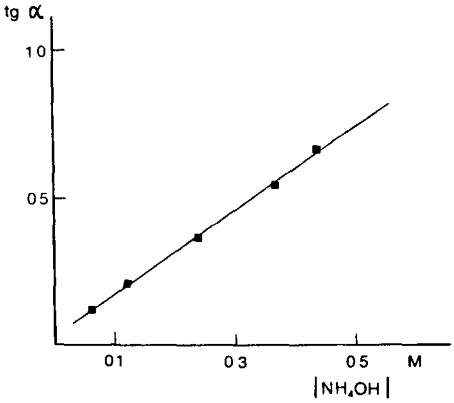

Fig 2 Variation of NH_4OH concentration [TETA] = 0 26% $S = 50$ mV $V_0 = 80$ ml Addition of 0 2 ml 23 9% H_2O_2

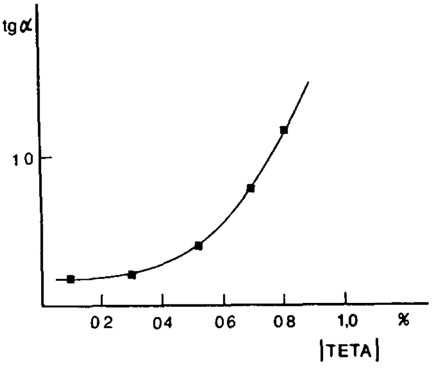

Fig. 3. Variation of TETA concentration. $[NH_4OH] = 0.122$ mol l^{-1}. $S = 50$ mV. $V_0 = 80$ ml. Addition of 0.2 ml 23.9% H_2O_2

Calibration graph

The calibration curve was obtained using several solutions with different quantities of Fe(III), with 10 ml of NH_4OH and 5 ml of 4.2% TETA, and diluting the mixture to a final volume of 80 ml. When the mixture had thermally stabilized, 0.2 ml of H_2O_2 of 23.9% was added with the precision syringe.

The application range of the method lies between (seven data points) 1.25 and 13 ng ml^{-1} of Fe(III) ($r = 0.9990$) with a relative standard deviation of 2.5% ($n = 8$) for 10 ng ml^{-1} of Fe(III) ($S = 50$ mV).

Interferences study

It is known that a lot of metal ions catalyze this reaction. In petroleum products the iron content is lower than the V(V) and Ni(II) content, and

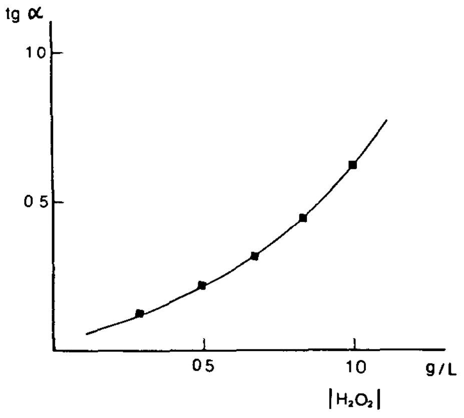

Fig. 4. Variation of H_2O_2 concentration. $[TETA] = 0.26\%$. $[NH_4OH] = 0.122$ mol l^{-1}. $S = 50$ mV. $V_0 = 80$ ml

similar to or higher than the content of all other metal ions (e g Cu(II), Co(II), Na(I),) We have studied the limit of sensitivity of these metal ions in order to apply this method to the determination of Fe(III) in petroleum products

Only Mn(II) interferes at low levels (0 1 ppb), but that is not a problem for the determination of iron in petroleum products, since the content of Mn(II) is generally much lower that the iron one

All other metal ions normally found in petroleum products only interfere at concentrations of 2500, or more, times the iron concentration (for example, Cu(II) > 30 ppm, V(V) > 25 ppm, Co(II) > 25 ppm and Ni(II) > 50 ppm) But the ratio of these metal ions concentrations in petroleum products, with respect to the iron concentration, is much lower than the above mentioned

For these reasons, we can conclude that the proposed thermometric method could be applied to the determination of Fe(III) in petroleum products with no significant interference

Determination of Fe (III) in petroleum products

The kinetic–thermometric method studied has been applied to determine Fe(III) in several petroleum products fuel oil, vacuum residue Isomax residue, GOLV (light vacuum gas oil) and GOPV (heavy vacuum gas oil) These determinations have been carried out by AAS and by the kinetic–thermometric technique proposed in this work The results are shown in Table 1

All these samples have been provided by EMP (Tarragona), and their Fe(III) content depends on the fuel origin and previous treatments

CONCLUSIONS

The thermometric method proposed in this work is more sensitive than the AAS method, and needs a lower quantity of sample to mineralize This

TABLE 1

Determination of Fe(III) in several samples

Sample	Average weight of sample/ volume of final aqueous solution	AAS method (mg kg^{-1}) [a]	Thermometric method (mg kg^{-1}) [a]
Fuel oil 1	33 g (50 ml)$^{-1}$	2 8 ±0 4	2 9 ±0 6
Fuel oil 2	26 g (50 ml)$^{-1}$	1 8 ±0 2	1 6 ±0 3
Vacuum R	30 g (50 ml)$^{-1}$	4 2 ±0 5	4 3 ±0 5
Isomax R	150 g (5 ml)$^{-1}$	0 07±0 02	0 10±0 05
GOLV	150 g (5 ml)$^{-1}$	0 32±0 08	0 36±0 10
GOPV	200 g (5 ml)$^{-1}$	0 17±0 07	0 20±0 09

[a] Mean values for the determination of three mineralization replicates of each sample

advantage produces an important economy of time in the mineralization step No interferences for the proposed kinetic–thermometric method have been found when it is applied to petroleum products

The low cost of the apparatus used, ease of handling, and the impossibility of poisoning the isolated transducer make this technique very competitive with respect to the official standard method

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