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# THERMOMETRIC STUDY OF THE BROMATE–IODIDE REACTION CATALYSED BY Mo(VI)

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## ABSTRACT

A thermometric method to determine $Mo^{VI}$, based on its catalytic effect on the iodide oxidation by bromate in a Landolt-type system, was studied.

The optimum concentrations of bromate, iodide, ascorbic acid and pH were determined and the reaction rate was obtained graphically from the temperature–time curve.

For a given concentration of reactants, the extent of bromate reduction is proportional to the $Mo^{VI}$ concentration. Concentrations in the range 12–30 ppm can be determined with a relative standard deviation of 2.5% ($n = 8$, 15 ppm $Mo^{VI}$).

The method was applied to determine $Mo^{VI}$ in hydrodesulphuration catalysts.

## INTRODUCTION

Several reactions catalysed by $Mo^{VI}$ have been studied: $H_2O_2$ with $I^-$ [1,2], $KBrO_3$ with *p*-phenetidine [3], $Ti^{III}$ with malachite green [4], $H_2O_2$ with rubeanic acid [5], etc. One of the best known, used in several investigations for the determination of molybdenum, is the Landolt-type system iodide–bromate–ascorbic acid [6,7].

$$BrO_3^- + 6I^- + 6H^+ \xrightarrow{Mo^{VI}} Br^- + 3H_2O + 3I_2$$

$$I_2 + \text{ascorbic acid} \rightarrow 2HI + \text{dehydroascorbic acid}$$

This reaction was originally studied spectrophotometrically by following the formation of iodine [8,9]; however, this is an exothermic reaction and it can also be followed thermometrically [6]. In both cases it is possible to use this reaction to determine molybdenum. It is known that this reaction is catalysed by several metals, e.g. vanadium [10], osmium [11], etc. In this

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work, a thermometric method to determine molybdenum was optimized, and it was applied to quantify this element in hydrodesulphuration catalysts.

## EXPERIMENTAL

### *Apparatus*

The thermometric system has been described elsewhere [12–15]. It is composed of an adiabatic nylon cell, a stirrer, a rapid response thermistor of the thermometer type (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 reagent addition into the thermometric cell.

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

### *Reagents*

$Mo^{VI}$ solution (100 ppm) was prepared by dissolving $Mo_7O_{24}(NH_4)_6 4H_2O$ (R.A., Probus) in distilled water. More dilute solutions were prepared daily. Ascorbic acid solution (0.1 M) was prepared by dissolving L(+)-ascorbic acid (R.A., Panreac) in distilled water. Bromate solution (1 M) was prepared by dissolving $NaBrO_3$ (R.A., Panreac) in distilled water. Iodide solution (1 M) was prepared by dissolving KI (R.A., Probus) in distilled water. Sulphuric acid solution (0.75 M) was prepared by dissolving sulphuric acid (36 M) (R.A., Probus) in distilled water.

All reagents were of analytical grade. The solutions were standardized by literature methods [16] and were stored at $20 \pm 1$ ° C.

### *Procedure*

Several assays were carried out to obtain a reproducible method for determining the thermometric curves; the procedure established was as follows.

$NaBrO_3$ solution (5 ml; 0.1 M), ascorbic acid solution (7 ml; 0.1 M), sulphuric acid solution (1 ml; 0.75 M), a determined quantity of catalyst and distilled water (to a final volume of 70 ml) were placed in the thermometric cell. When the system was thermally stable, KI solution (0.7 ml; 1 M) was added with a syringe to start the reaction.

Another procedure involving the addition of the $NaBrO_3$, ascorbic acid, KI and catalyst solutions initially, followed by the $H_2SO_4$ solution after thermal stability has been reached produces non-reproducible results; this is because the reaction starts slowly before the $H_2SO_4$ addition due to the weak acidity of the media.

### *Mineralization method*

The thermometric method was used to determine the molybdenum content of hydrodesulphuration catalysts. The sample was treated with HCl and the solution was diluted with distilled water. The catalysts analysed contained molybdenum or molybdenum and cobalt.

## RESULTS AND DISCUSSION

The different variables that affect the catalytic action of $Mo^{VI}$ on the bromate–iodide reaction were optimized in order to achieve a maximum sensitivity and a wide application range.

First of all, the influence of ascorbic acid on the exothermic reaction was studied. In Fig. 1, it can be seen that when ascorbic acid is present, there is a linear response ($\Delta T/t$), which is not obtained when ascorbic acid is absent.

In Figs. 2 and 3, the tan $\alpha$ values obtained are plotted as a function of iodide and bromate concentrations, respectively. An iodide concentration of 0.01 M and a bromate concentration of 0.07 M are the optimum values obtained to give a wide application range and a maximum difference between the catalysed reaction and the blank experiments.

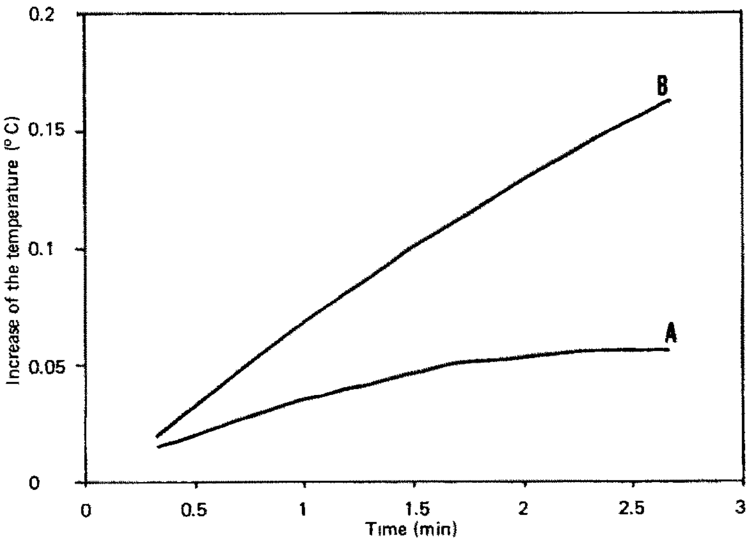

Fig. 1. Effect of ascorbic acid on the catalytic reaction ($[BrO_3^-] = 0.071$ M; $[H_2SO_4] = 0.006$ M; $[I^-] = 0.014$ M; [Mo(VI)] = 7.14 ppm): curve A, blank; curve B, [ascorbic acid] = 0.014 M.

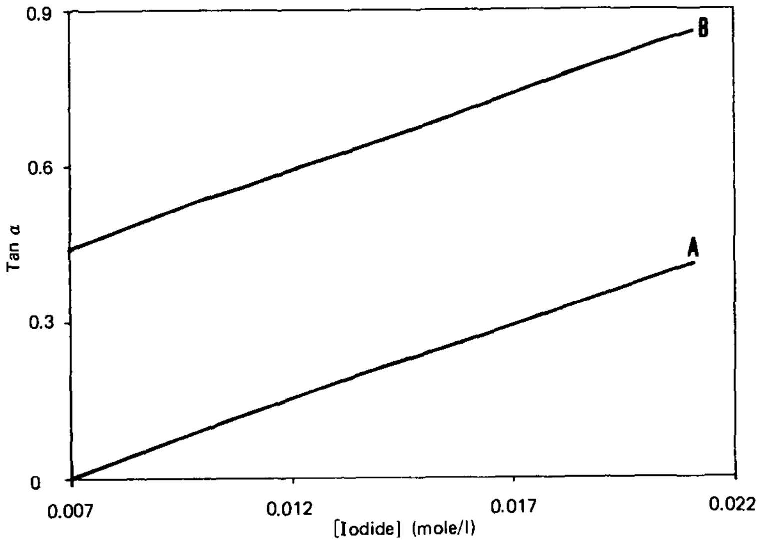

Fig. 2. Influence of iodide concentration on the initial rate ($[BrO_3^-] = 0.071$ M; $[H_2SO_4] = 0.006$ M; [ascorbic acid] = 0.014 M): curve A, blank; curve B, [Mo(VI)] = 7.14 ppm.

In Fig. 4 the influence of ascorbic acid concentration on the reaction rate is shown. It can be seen that the tan $\alpha$ value is at a maximum for a 1 : 1 ascorbic acid : iodide stoichiometry; this suggests the formation of an intermediate with a maximum catalytic activity value in these conditions. This maximum value (0.01 M) was chosen as the optimum ascorbic acid con-

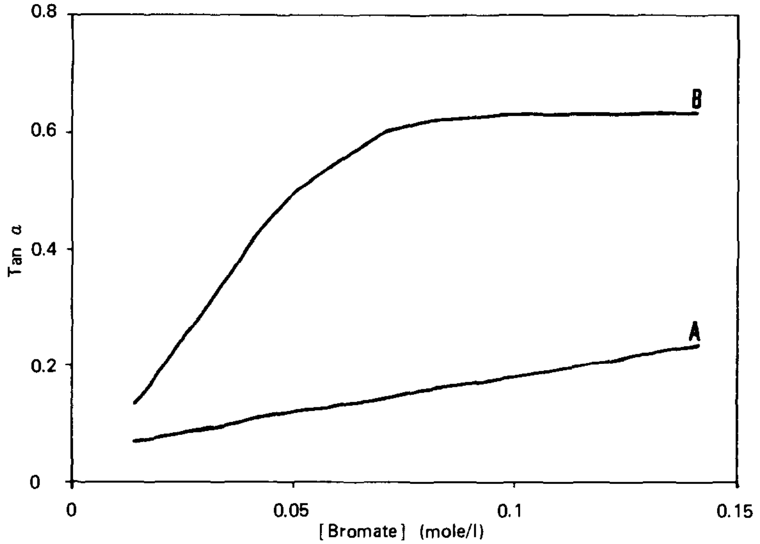

Fig. 3. Influence of bromate concentration on the initial rate ($[H_2SO_4] = 0.006$ M; [ascorbic acid] = 0.014 M; $[I^-] = 0.014$ M): curve A, blank; curve B, [Mo(VI)] = 7.14 ppm.

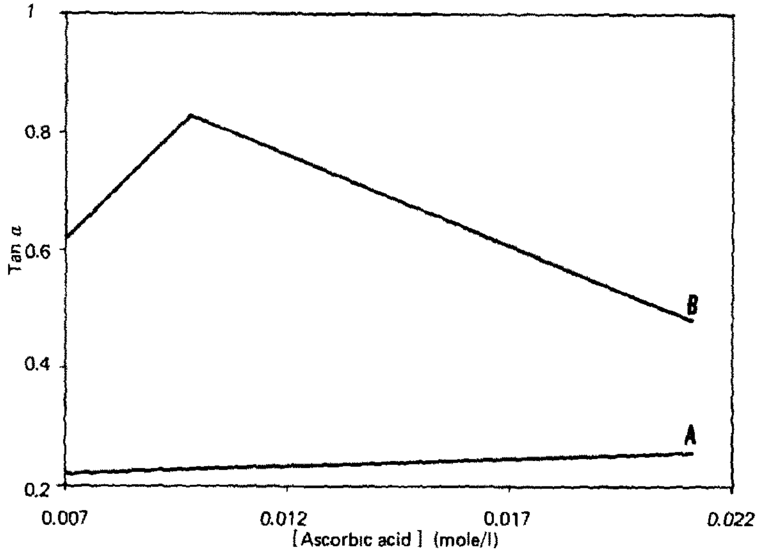

Fig. 4. Influence of ascorbic acid concentration on the initial rate ($[BrO_3^-] = 0.071$ M; $[I^-] = 0.01$ M; $[H_2SO_4] = 0.006$ M): curve A, blank; curve B, [Mo(VI)] = 7.14 ppm.

centration. On the basis of these facts and the results obtained for the reduction of $Cr^V$ with ascorbic acid [17], the formation of an $Mo^{VI}$ complex with a 1 : 1 iodide : ascorbic acid stoichiometry can be proposed, which can change to an $Mo^{IV}$ species, reducing bromate to bromide.

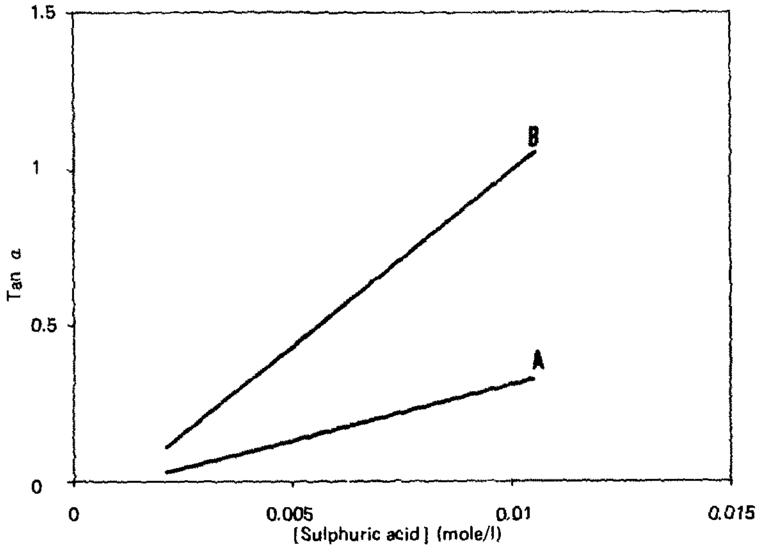

Fig. 5. Influence of sulphuric acid concentration on the initial rate ($[BrO_3^-] = 0.071$ M; $[I^-] = 0.01$ M; [ascorbic acid] = 0.01 M): curve A, blank; curve B, [Mo(VI)] = 7.14 ppm.

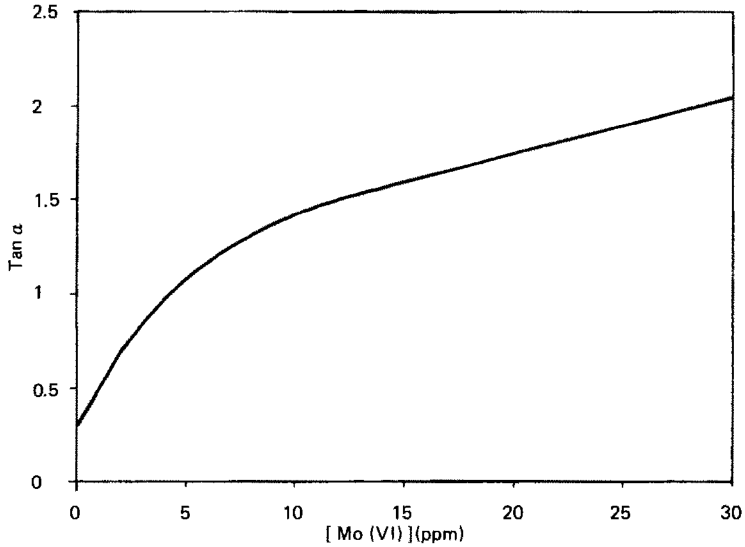

Fig. 6. Study of the linearity of the response ($[BrO_3^-] = 0.07$ M; [ascorbic acid] = 0.01 M; $[I^-] = 0.01$ M; $[H_2SO_4] = 0.01$ M).

The study of the influence of the sulphuric acid on the reaction rate (Fig. 5) shows that the sensitivity increases with increasing sulphuric acid concentration. In addition, an increase in the tan $\alpha$ values corresponding to the blank experiments is noted, probably due to the presence of impurities in the sulphuric acid which catalyse the reaction. An optimum value of 0.01 M sulphuric acid concentration was chosen to carry out the molybdenum determinations.

Finally, using optimum conditions, the calibration curve was obtained (Fig. 6). A linear response between 12 and 30 ppm of $Mo^{VI}$ can be seen; this interval was used in subsequent determinations. The analytical procedure was established with a 2.5% relative standard deviation for 15 ppm of molybdenum ($n = 8$).

## INTERFERENCES

A study was carried out to determine the possible interferences in the proposed method. The determinations were performed with a 14 ppm $Mo^{VI}$ solution in the presence of 100 ppm of the following cations: $Ca^{II}$, $Ba^{II}$, $Sr^{II}$, $Na^{I}$, $K^{I}$, $Pb^{II}$, $Cd^{II}$, $As^{III}$, $Sb^{III}$, $Sn^{II}$, $Ni^{II}$, $V^{V}$, $Cr^{III}$, $W^{VI}$, $Cu^{II}$, $Fe^{III}$, $Mn^{VI}$, $Co^{III}$ and $Ru^{III}$.

Only $V^{V}$ and $Ru^{III}$ interfered. In Figs. 7 and 8 the curves obtained for various $Ru^{III}$ and $V^{V}$ concentrations are shown.

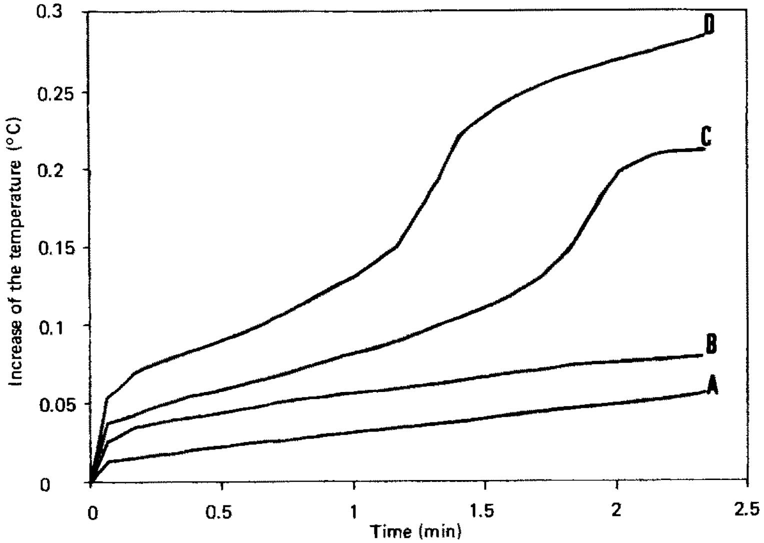

Fig. 7. Thermometric curves of the $Ru^{III}$ catalysed reaction ($[BrO_3^-] = 0.07$ M; $[I^-] = 0.01$ M; [ascorbic acid] = 0.01 M; $[H_2SO_4] = 0.01$ M): curve A, [Ru(III)] = 3.9 ppm; curve B, [Ru(III)] = 7.8 ppm; curve C, [Ru(III)] = 9.76 ppm; curve D, [Ru(III)] = 13.7 ppm.

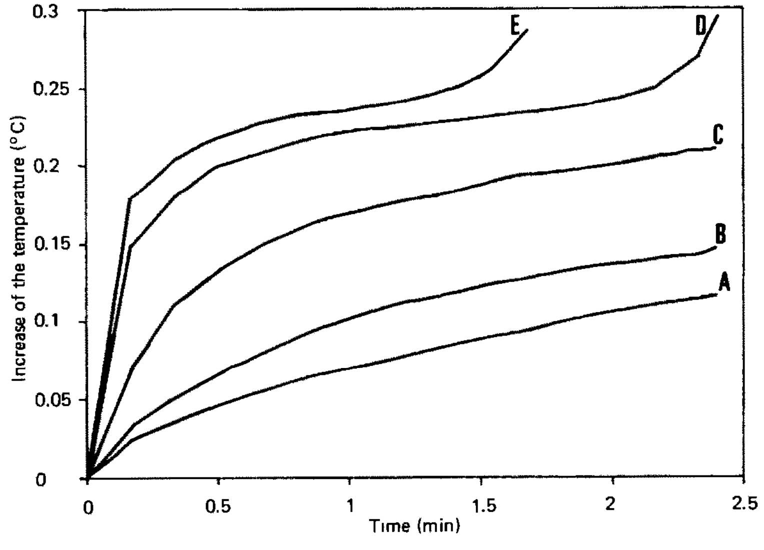

Fig. 8. Thermometric curves of the $V^V$ catalysed reaction ($[BrO_3^-] = 0.07$ M; $[I^-] = 0.01$ M; [ascorbic acid] = 0.01 M; $[H_2SO_4] = 0.01$ M): curve A, [V(V)] = 2.8 ppm; curve B, [V(V)] = 5.5 ppm; curve C, [V(V)] = 14 ppm; curve D, [V(V)] = 56 ppm; curve E, [V(V)] = 70 ppm.

TABLE 1

Results obtained by both methods

| | Thermometric method (% molybdenum) | Atomic spectrophotometry (% molybdenum) |
|---|---|---|
| Catalyst 1 | $2.5 \pm 0.2$ | $2.4 \pm 0.1$ |
| Catalyst 2 | $6.0 \pm 0.4$ | $5.8 \pm 0.2$ |

Values are the mean of three determinations.

In both cases, the different zones on the curves can be related to redox processes involving the metallic ions. Thus, for $V^{V}$ it has been well established [18] that

$$2HVO_3 + 3KI + 3H_2SO_4 \rightleftharpoons 2VOSO_4 + KI_3 + K_2SO_4 + 4H_2O \quad (1)$$

$$10VOSO_4 + 2KBrO_3 + 14H_2O \rightleftharpoons 10HVO_3 + Br_2 + KSO_4 + 9H_2SO_4 \quad (2)$$

For ruthenium, the initial presence of different oxidized species, in particular $Ru^{III}$ and $Ru^{IV}$ (in agreement with the chemistry in solution of these ions [18–20]) must be taken into account.

## APPLICATION

The method was applied to determine molybdenum in two hydrodesulphuration catalysts, and the results are compared with those obtained by atomic absorption spectrophotometry in Table 1.

## ACKNOWLEDGEMENT

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