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THE CATALYTIC-THERMOMETRIC DETERMINATION OF MOLYBDENUM IN STEELS BASED ON THE HYDROGEN PEROXIDE–IODIDE INDICATOR REACTION

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ABSTRACT

The Mo^{VI}-catalysed hydrogen peroxide–iodide reaction has been optimised for thermometry in an HCl medium using the initial slope method. The substitution of sodium perborate by H_2O_2 and the conversion of the reaction to a process showing a Landolt effect are considered and discussed. The linear range extended from 0.2 μg Mo^{VI} ml^{-1} to 1.2 μg Mo^{VI} ml^{-1} with a detection limit of 0.06 μg Mo^{VI} ml^{-1}. Interferences were also studied. The optimised procedure was applied to the evaluation of molybdenum in steels after extraction with α-benzoinoxime in chloroform.

INTRODUCTION

Yatsimirskii and Afanas'eva [1] were the first researchers to propose the determination of molybdenum using the catalytic action of molybdate ions on the reaction between hydrogen peroxide and potassium iodide in acidic medium

$$H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O \qquad (1)$$

The rate of the reaction is a function of the concentrations of H_2O_2, I^- and acid. These concentrations may be considered constant near the start of the reaction, when a large excess of the three species is used. Under these conditions, the reaction rate is proportional to the concentration of catalyst. Spectrophotometry (directly following the absorption of triiodide ion or after reaction with starch or variamine blue) [1–14], potentiometry with an iodide-selective electrode [15–18], amperometry [19,20] and conductimetry [17] have all been used for monitoring the reaction.

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Thermometry is particularly appropriate for those redox reactions which are highly exothermic. In thermometry, a highly coloured background and the presence of precipitates do not interfere. Feys et al. [21] have demonstrated the possibility of evaluating Mo^{VI} by using the H_2O_2–I^- indicator reaction and the initial slope method. However, the procedure was presumably not optimised as sulphuric acid was used to acidify the solutions. Sulphuric acid is not suitable for thermometry because of its high heat of dilution. Later, Gaál et al. [22] described a catalytic-thermometric procedure to determine Mo^{VI}, which uses the Landolt effect produced by ascorbic acid on the reaction between H_2O_2 and I^-. The determination was performed at pH 4.5 in an acetate buffer.

In this work, the Mo^{VI} catalysed H_2O_2–I^- reaction, performed in an HCl medium using the initial slope method, has been optimised for thermometry. The substitution of sodium perborate by H_2O_2, and the conversion of the reaction to a process showing a Landolt effect are also considered and discussed. The optimised procedure was applied to the evaluation of molybdenum in steels after extraction with α-benzoinoxime in chloroform.

EXPERIMENTAL

Reagents

The stock solution (993 μg Mo^{VI} ml^{-1}), prepared from $Na_2MoO_4 \cdot 2H_2O$, was back-titrated with EDTA in the presence of xylenol orange, after addition of an excess of Pb^{II} to the hot solution. Other solutions were: 0.024 M H_2O_2, 0.02 M $NaBO_3 \cdot 4H_2O$, 2 M KI, 0.04 M ascorbic acid and 1% α-benzoinoxime in chloroform. The H_2O_2, KI and α-benzoinoxime solutions were prepared daily. Ultrapure water was used throughout (Barnstead NANOpure II).

Apparatus

The thermometric system, provided with a constant d.c. power supply and a Wheatstone bridge, was constructed according to the design of Lumbiarres et al. [23]. The experiments were performed in a thermostated room at 20.0 ± 0.1°C. The polypropylene reaction cell, having a 30 ml capacity and 0.5 mm thick walls, was suspended in a 1 l Dewar vessel as shown in Fig. 1. Injection was performed through a 2 ml Teflon coil also suspended inside the Dewar in order to minimise the temperature mismatch between the injected solution and the cell. A Dispensette Brand model 707601 dosifier was used. The glass-sealed thermistor had a nominal resistance of 5 kΩ at 25°C. The applied voltage was 1.000 ± 0.001 V. A response of 15.27 mV

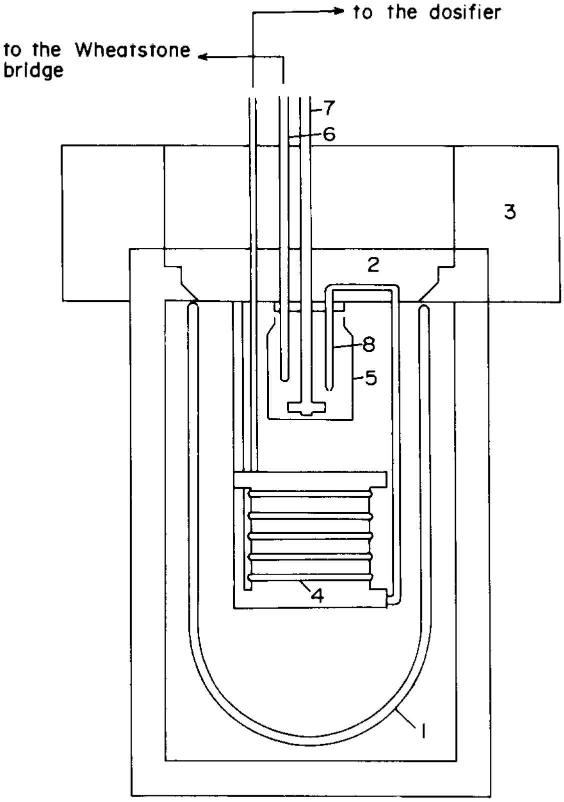

Fig. 1. Thermometric cell and isolation system: 1, Dewar vessel; 2, plastic cover; 3, polystyrene block, 4, teflon coil; 5, thermometric cell; 6, thermistor; 7, stirrer; 8, tip of the injection tube.

$°C^{-1}$, corresponding to a 305.4 mm $°C^{-1}$ recorder-pen deflection was obtained.

Procedure for the determination of molybdenum in steels

An appropriate amount of the steel sample was dissolved in 3 M H_2SO_4. Some drops of concentrated HNO_3 were added and heat was applied until elimination of nitrous vapours. An aliquot with a maximum molybdenum content of 140 μg was taken, diluted to 40 ml, acidified to pH 1 and 1 ml of 1% NH_4F was added. Molybdenum was extracted three times with 5 ml of 1% α-benzoinoxime and back-extracted from the combined organic phase with two 5 ml portions of 0.5 M ammonia, neutralised to pH 5–6 with HCl and diluted to 50 ml in a volumetric flask. A 5 ml aliquot was pipetted into the thermometric cell together with 5 ml of 0.4 M HCl, 5 ml of 0.024 M H_2O_2 and 5 ml of water. Finally, 1 ml of 2 M KI was injected and the thermometric curve was recorded for 1 min (chart speed 10 cm min^{-1}). The initial slope of a blank prepared in the absence of catalyst was subtracted from the initial slope of the sample solutions. Triplicate experiments were performed.

RESULTS AND DISCUSSION

Optimisation of experimental conditions

The order in which the reagents were mixed did not significantly affect the initial rate of the H_2O_2–I^- reaction. However, injection of KI rather than H_2O_2 was preferred in order to avoid the formation of bubbles in the injection tube.

When 5 ml of 0.4 N H_2SO_4 were used instead of HCl, almost the same slope was obtained, with and without molybdenum, the temperature rise being, therefore, mainly due to the dilution heat of the acid. A much greater sensitivity and a lower blank signal were obtained by using HCl at the same catalyst concentration. The influence of the HCl concentration on the sensitivity, after subtraction of the blank slope, is shown in Fig. 2. A maximum was obtained at 0.1 M HCl. Sensitivity was also optimal for 6×10^{-3} M H_2O_2, as shown in Fig. 3. With these conditions, the slopes of the blanks were rather low.

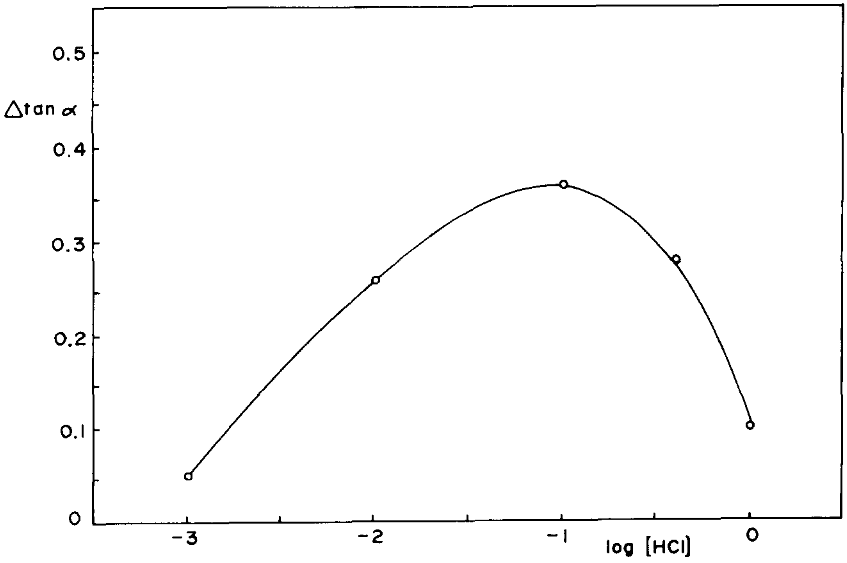

Fig. 2. Effect of the concentration of HCl (4.5×10^{-3} M H_2O_2, 5×10^{-2} M KI, 0.5 μg Mo^{VI} ml^{-1}) (Δ tan α is given in cm s^{-1} in all figures).

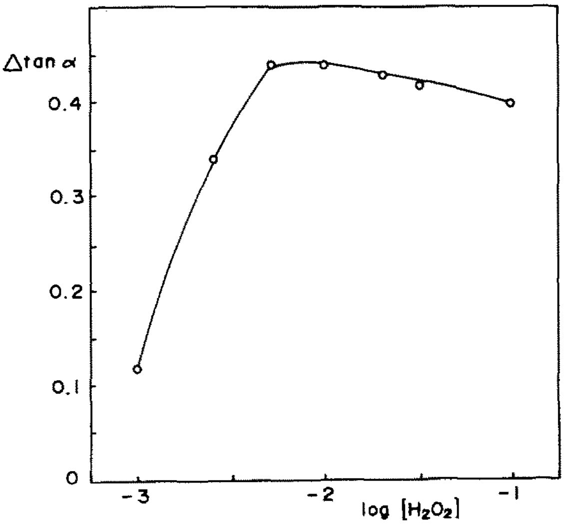

Fig. 3. Effect of the concentration of hydrogen peroxide (5×10^{-2} M KI, 0.1 M HCl, 0.5 μg Mo^{VI} ml^{-1}).

The Δ tan α versus log[KI] curve (Fig. 4) does not show a maximum in the concentration range studied, having an exponential shape. A concentration of 0.1 M KI in the cell was chosen corresponding to the injection of 1 ml of 2 M KI. Thus, a satisfactory sensitivity can be achieved with moderate reagent expense.

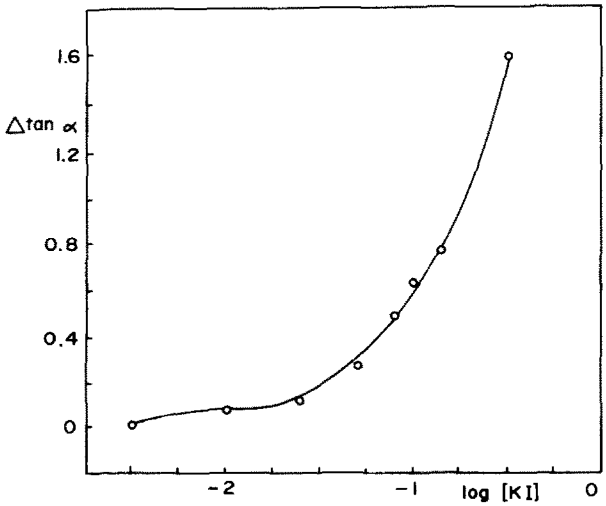

Fig. 4. Effect of the concentration of iodide (6×10^{-3} M H_2O_2, 0.1 M HCl, 0.5 μg Mo^{VI} ml^{-1}).

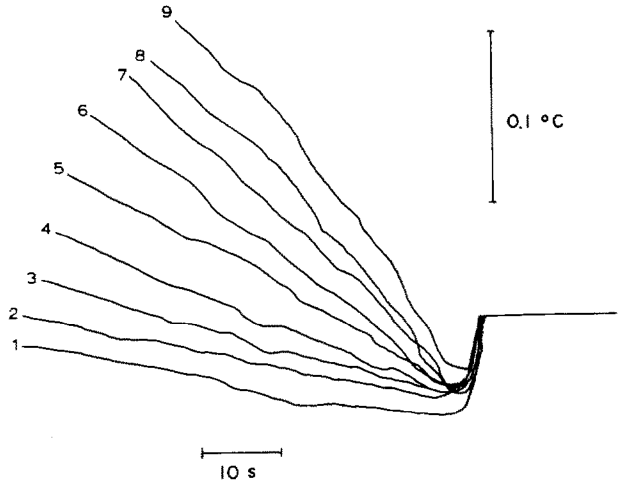

Fig. 5. Thermometric curves (6×10^{-3} M H_2O_2, 0.1 M KI, 0.1 M HCl). Concentration of Mo^{VI} in μg Mo^{VI} ml^{-1}: 1, 0.03; 2, 0.05; 3, 0.1; 4, 0.2; 5, 0.4; 6, 0.6; 7, 0.8; 8, 1.0; and 9, 1.2.

Analysis

Figure 5 shows several thermokinetic curves corresponding to different concentrations of Mo^{VI}. After an initial decrease, owing to the endothermic dilution of the injected KI, a linear increase of temperature is observed. The corresponding calibration curve is shown in Fig. 6. The following equation was obtained by linear regression

$$y = 0.003 + 1.006C_{Mo} \qquad r = 0.9996 \qquad (2)$$

which corresponds to a sensitivity of 0.033° C min^{-1} (μg $Mo^{VI})^{-1}$ ml^{-1}. The linear range extended from 0.2 μg Mo^{IV} ml^{-1} to 1.2 μg Mo^{VI} ml^{-1} with a detection limit of 0.06 μg Mo^{VI} ml^{-1} (10 blanks, 3 s criterion). The coefficient of variation was 6.7% and 2.5% for 0.2 μg Mo^{VI} ml^{-1} and 1 μg Mo^{VI} ml^{-1}, respectively (five replicates).

Substitution of sodium perborate by hydrogen peroxide

In acidic medium, sodium perborate gives perboric acid which behaves as a mixture of H_2O_2 and boric acid. The influence of the concentrations of HCl, perborate and KI were similar to those observed with H_2O_2, the optimal conditions being 0.1 M HCl, 9×10^{-3} M perborate and 0.1 M KI. The linear range was 0.1 μg Mo^{VI} ml^{-1}–1.0 μg Mo^{VI} ml^{-1}, the sensitivity was 0.031° C min^{-1} (μg $Mo^{VI})^{-1}$ ml^{-1} and the detection limit was 0.03 μg Mo^{VI} ml^{-1}. The coefficient of variation was 5% and 3.5% for 0.3 μg Mo^{VI} ml^{-1} and 0.75 μg Mo^{VI} ml^{-1}, respectively. Both reagents, therefore, give similar figures of merit, the only probable advantage in the use of perborate being the larger stability of the solutions.

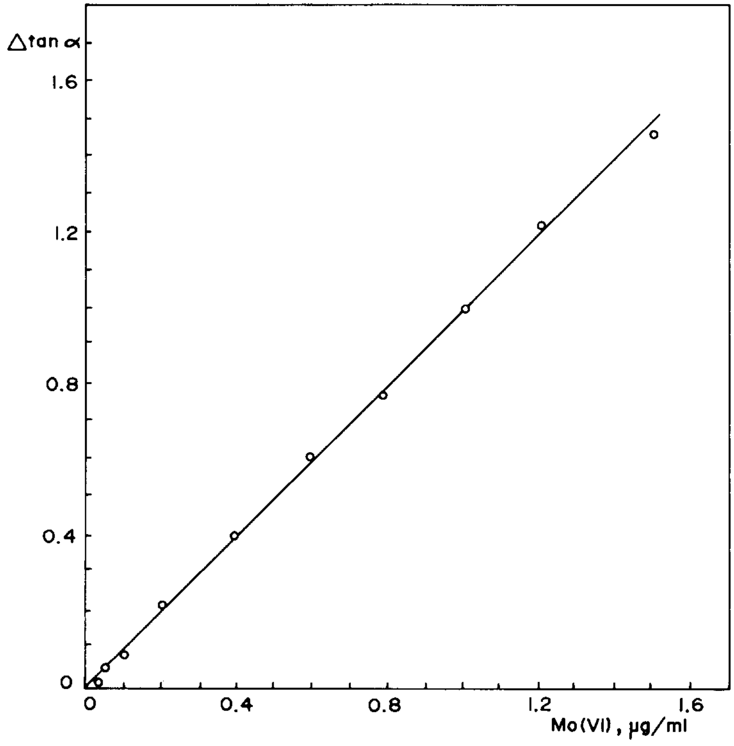

Fig. 6. Calibration plot.

Use of the Landolt effect

Experiments similar to those of Gaál et al. [22] were performed in 0.1 M HCl medium. Hydrogen peroxide and HCl in the concentrations given above were introduced into the thermometric cell, together with varying concentrations of Mo^{VI}. A 1 ml aliquot of a 2 M KI–0.04 M ascorbic acid solution was then injected. In this way, the concentration of ascorbic acid in the cell was a third that of H_2O_2. The chart speed was lowered to 2 cm min^{-1} and the change of temperature produced was registered during a 3–10 min period.

The thermometric curve has two well-defined linear sections (Fig. 7), the first (section A) corresponding to reaction (1) and to the oxidation of ascorbic acid to dehydroascorbic acid by iodine, which proceed simultaneously. When ascorbic acid is totally oxidised, iodine begins to appear in the solution and the temperature rise (section B) is then due to reaction (1) alone. The reciprocal of the length of section A (induction period) is proportional to the concentration of Mo^{VI}. The following equation was obtained by linear regression

$$1/t = 0.087 + 2.758C_{Mo} \qquad r = 0.9999 \qquad (3)$$

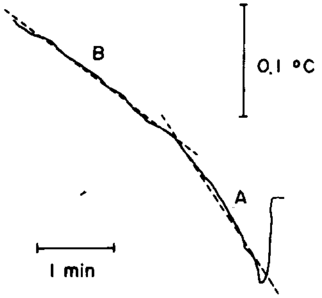

Fig. 7. Thermometric curve showing the Landolt effect (6×10^{-3} M H_2O_2, 0.1 M KI, 2×10^{-3} M ascorbic acid, 0.1 M HCl, 0.2 μg Mo^{VI} ml^{-1}).

with t in s and C_{Mo} in μg Mo^{VI} ml^{-1}. The linear range extended between 0.05 and 0.4 μg Mo^{VI} ml^{-1}. These values are one order of magnitude lower than those obtained by Gaál et al. (1–10 μg Mo^{VI} ml^{-1}), which may result from differences in the experimental conditions, especially the pH of the solutions. However, in comparison with the initial slope method, the use of the Landolt effect did not lead to any significant improvement; on the contrary, longer reaction times were required.

Interference

The effect of diverse ions on the determination of 0.75 μg Mo^{VI} ml^{-1} was investigated. The acid solutions of Sn^{II}, Sb^{III}, Bi^{III}, Fe^{II}, Fe^{III}, Ti^{IV} and Nb^{V} were previously neutralised in the cell. Thus, when 5 ml of 0.4 M HCl was added, the appropriate pH was achieved. The results are given in Table 1, where the concentrations are related to the volume introduced in the thermometric cell before the injection of iodide.

TABLE 1

Effect of foreign ions

Foreign ion	Maximum amount tolerable [a] (μg ml^{-1})
Ag^{I}, Ca^{II}, Ba^{II}, Mg^{II}, Sr^{II}, Be^{II}, Ni^{II}, Co^{II}, Zn^{II}, Pb^{II}, Cd^{II}, Hg^{II}, Mn^{II}, Cr^{III}, Al^{III}, Bi^{III}, Nb^{V}	80 [b]
Sb^{III}	64
F^{-}	32
Cu^{II}	24
Ti^{IV}	8
Fe^{III}, V^{IV}, Zr^{IV}, Cr^{VI}	4
Fe^{II}, Sn^{II}, V^{V}	1.6
W^{VI}	0.32

[a] Concentrations corresponding to ≤ 5% error in the determination of 0.75 μg Mo^{VI} ml^{-1}.
[b] Maximum concentration examined.

The interference of Fe^{II}, Fe^{III}, V^{V}, Zr^{IV} and W^{VI} was positive owing to their catalytic action on the H_2O_2–I^- reaction (V^{IV} is oxidised to V^{V}). The negative interferences probably resulted from the formation of complexes with I^- (Sb^{III}), H_2O_2 (Ti^{IV}) and Mo^{VI} (F^-), or from the oxidation of H_2O_2 (Cr^{VI}).

The interference of Fe^{III} can be reduced by masking with EDTA [24], DCTA or F^- [8]. The interference of Cr^{VI} can be removed by reduction with H_2O_2 and evaporation of the sample solution to dryness [7]. However, most of the interfering ions can be removed by ion-exchange in a Dowex 50W-X8 column [25] or by extraction of Mo^{VI} with α-benzoinoxime in chloroform in the presence of F^-, followed by back-extraction with ammonia [2].

Determination of molybdenum in steels

The thermometric procedure with H_2O_2 described above was applied to the determination of molybdenum in steels. The extraction of Mo^{VI} with α-benzoinoxime was quantitative up to 140 μg of molybdenum (see procedure). The removal of the main interferents present in steels (iron, chromium, vanadium and tungsten) was checked with synthetic samples. Calibration was performed with Mo^{VI} solutions without extraction. The results obtained with three steel standards are given in Table 2.

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TABLE 2

Evaluation of molybdenum in steels

Sample reference	Certified composition (%)	Molybdenum found (%)
N-56 [a]	Mo 0.953, C 0.865, Si 0.318 Mn 0.205, P 0.0242, S 0.0049, Cr 4.231, Co 2.730, Ni 0.220, V 1.981	1.07 ±0.04
F-174 [b]	Mo 0.190, C 0.372, Si 0.270, Mn 0.495, P 0.0171, S 0.01, Cr 1.606, Ni 0.105, Al 1.026	0.180±0.003
64-b [c]	Mo 5.0, C 0.9, Cr 4.5, V 2.0, W 7.0	5.6 ±0.2

[a] N-56, Bundessanstalt für Material Prüfung Berlin-Dahlem, West Germany.
[b] F-174, Instituto del Hierro y del Acero, Madrid, Spain.
[c] 64-b, Bureau of Analysed Samples Ltd., Gt. Britain.

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