USE OF HYDROGEN PEROXYDE AS ANALITICAL REAGENT IN A CONTINUOUS FLOW-ASSEMBLY

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Summary

The use of hydrogen peroxide as oxidative reagent is an general procedure in the analytical chemistry. However, its use in a continuous-flow manifold is a source of practical inconvenients and the complete destruction of the reagent excess before to flow through the detector flow-cell is required. In this article a flow manifold is studied and proposed for the destruction of hydrogen peroxide after being used as oxidative reagent. The excess of reagent is destroyed and removed from the flow-injection manifold by means of a metallic copper reactor which acts as catalyst in the decomposition of H_2O_2 and a home made debbubler.

Key-words: Hydrogen peroxide, FIA, spectrophotometry.

1. Introduction

A certain number of analytical procedures, mainly in the field of drug analysis [1, 2, 3], are based on the use of hydrogen peroxide as oxidant, were the excess of reagent is destroyed by boiling the solution prior to the spectrophotometric monitoring. Altough hydrogen peroxide is colourless and transparent in the visible region, but highly absorbant in the UV range. On the other hand, the scarce use of hydrogen peroxide in continuous flow procedures is also due to the problems arising from the continuous and irreproducible bubbling of oxygen. Those bubbles alter the flow and remain in different parts of the assembly even in the flow-cell, changing the active surface of electrodes (electrochemical detection) or blocking the flow or altering the light path (spectrophotometric and fluorimetric detection). A simple debubbler is not enough due the bubble formation even inside the detector flow-cell. The well known decomposition of H_2O_2 into H_2O and O_2 occurs via complicated reaction mechanisms which are

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depending on several parameters as reaction media, temperature, pressure, contact surfaces, etc [4, 5, 6]. A former short communication from this lab was dealing with the hydrogen peroxide destruction using a solid-phase reactor of pirolusite from natural origin [7].

This paper deals with the study of the use of H_2O_2 as reagent in a continuous-flow manifold. After acting as oxidant the excess of H_2O_2 is completely destroyed by means of a solid-bed reactor (immobilised metallic copper) which acts as catalyst in the decomposition of the oxidant and prior to monitoring with a spectrophotometric detector. The liberated gas in the flowing stream is removed as in a fast and efficient way previously to the detector entrance by using a debubbler placed between the bed reactor and the detector. The assays aimed to destruction and removing of the hydrogen peroxide were performed with the aid of a spectrophotometric detection due to the high absorbance in the UV region.

2. Experimental

2.1. Reagents

Analytical-reagent grade chemicals were used unless indicated otherwise. H_2O_2 (Scharlau). The solid bed reactors containing MnO_2 (Panreac), $CuCO_3{\cdot}Cu(OH)_2{\cdot}2H_2O$ (Panreac) and PbO_2 (UCB) were prepared as described earlier [4, 5] with AL-100-A polyester resin solution (Reposa) containing low-molecular-weight polyester chains, a cobalt compound as activating agent of the reaction and methyl ethyl ketone as catalyst (Azko) were employed. Metallic copper (Probus) was used as immobilised catalitic reagent for the present purpose.

2.2. Flow-injection assembly

A single-channel continuous flow assembly (Fig.I) was used with the copper reactor between the injection valve and detector. The column was placed in a water-bath (Selecta) at 100 ℃. A Rheodyne Model 5041 sample injector and a Gilson Minipuls 2 pump were employed. The flow system was made of PTFE tubing of 0.8 mm i.d. and 1.5 mm i.d. for the manifold and reaction column, respectively. A home-made debubbler (two perspex bodies with connectors and a PTFE film as gas permeable membrane) was used to remove the bubbles produced due to the catalitic decomposition of H_2O_2 in the bed reactor. (For details see the Fig I). As detector was used a diode array spectrophotometer 8452A from Hewlett Packard provided with a flow-cell from Hellma 18 ul inner volume.

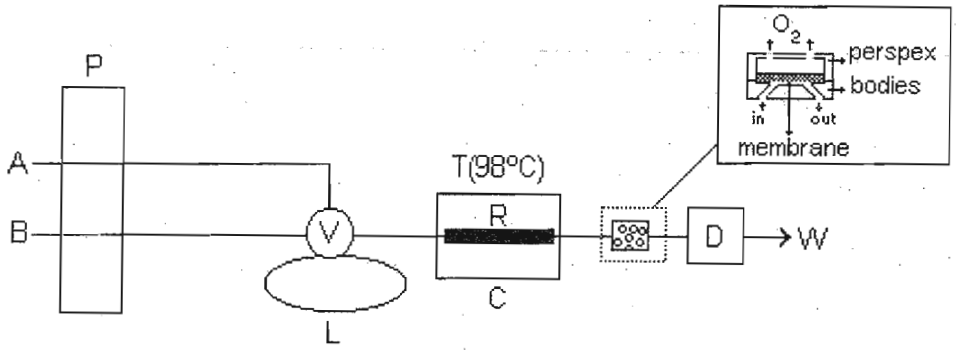

Figure I. Flow assembly for destruction of hydrogen peroxyde.
A, H_2O_2 solution; B, carrier; R, copper bed reactor; P, peristaltic pump; T, termostatic bath; C, debubbler; D, detector and W, waste

2.3. Preparation of the bed reactors

A suitable amount of metallic copper was ground in a coffee grinder and particles between 100 and 300 (m were selected by sieving. Then particles with suitable size were washed with diluted HCl and the surface activated with H_2O_2 (33%) during one hour. Finally, the copper particles were dried and the bed reactor was prepared by introducing the particles by means of a minifunnel with the aid of mechanical stirring into a PTFE tube of 1.5 mm i.d.

Solid bed-reactors containing MnO_2, $CuCO_3 Cu(OH)_2 2H_2O$, PbO_2 and Cu employed in preliminary studies were prepared as follows: a suitable amount of reagent was added to the polyester resin solution (the ratio reagent/resin was 1:1 (w/w) in all cases except for PbO_2 (2:1)). The mixture was homogenised by manual stirring and then ethyl methyl ketone was added and stirring was continued until the polymer became too rigid. The solid was dried for 2-3 hours at room temperature, then broken with a hammer and grinded in a coffee mill.; particles between 150 and 200 um were selected by sieving. The bed reactors were prepared by introducing the particles via a minifunnel with stirring into a PTFE tube of 1.5 mm of inner diameter and 25 cm long.

3. Results and discussion

The potential interference of excess oxidant in the detection step led us to attempt its on-line quantitative removal from the FIA system. For this purpose a manifold similar to that depicted in Fig. I was used provided with a spectrophotometer (due to high absorbance. The following elements were inserted between the injection valve and detector: a column containing the solid reagent used to decompose H_2O_2, immersed in a

thermostated bath at variable temperatures up to 80(C; and a debubbler located at the reactor exit intended to remove the bubbles formed, which might interfere with detection.

Hydrogen peroxide was decomposed in two different ways, namely: by oxidation with a powerful oxidant (PbO_2) and by the catalytic effect of copper or pirolusite on the reaction $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$. For this purpose, 25 cm long x 1.5 mm i.d. reactors containing particles in sizes from 150-200 um were used. PbO_2, MnO_2, $CuCO_3 \cdot Cu(OH)_2 \cdot 2H_2O$ and metal copper were immobilised on polyester resin in ratios of 2:1, 1:1, 1:1 and 1:1 (w/w), respectively, as described in the Exprimental section. Metal copper was also confined in the FIA manifold (natural immobilisation) after treatment of the surface of the copper turnings as described above. The column length used here was 12 cm.

Previous tests for H_2O_2 decomposition were performed in a continuous-flow assembly by using de-ionised water at a flow-rate of 1.4 ml/min as carrier, and injecting H_2O_2 solutions at concentrations between 0.01 M and 0.1 M.

In all cases, the decrease in the absorption peak for H_2O_2 (λ_{max}= 239 nm) relative to the signal obtained in the absence of column -the height of which was taken to be 100%- was used as the analytical signal. The results obtained are given in Table 1. The temperature used was dictated by the reactor efficiency observed in the preliminary experiments: the higher the efficiency was, the wider was the range studied.

As a rule, the reagent decomposition was non-quantitative except at high temperatures (80 °C) and low H_2O_2 concentrations; however, metal copper decomposed the hydrogen peroxide quantitatively at lower temperatures (60 °C) throughout the concentration range studied. Lead oxide was not used subsequently despite its excellent performance, event at room temperature, because it is reactive towards many drugs (or any other analite) due to its high oxidant power. On the other hand, $CuCO_3 \cdot Cu(OH)_2 \cdot 2H_2O$ was dissolved as the temperature was raised and the reactor life-time was abruptly shortened as a result, thus rendering it unusable above room temperature. The hydrogen peroxyde decomposition was always completed (copper reagent) for concentracions up to 0.1 mol l^{-1} without influence of the flow rate; for concentrations upper to 0.0 mol l^{-1} th influence of the flow-rate is relevant, at values upper 3.4 ml min^{-1} the proposed debubbler was not able to eliminate completly the evolved oxygen.

Several empirical studies were performed to test the analytical characteristics of the column (cooper reagent)-debubbler set. The life-span of the column was studied by forcing a solution containing hydrogen peroxyde 0.03 mol l^{-1} through the manifold during four hours. No variations were observed in the signal at λ_{max}= 239 nm. The contribution of this set to the dispersion of the sample was tested by injecting aliquotes of the pyrogalol red solution. The outputs from those injections were compared with the

Table I. Influence of the bed reactor on the decomposition of the excess of oxidant. In the table, diminution of the absorbance of H_2O_2 at 239 nm (%) compared with the observed signal without bed reactor (100%).

$[H_2O_2]$ M	t (20°C)				
	$CuCO_3^*$	Cu^*	Cu	MnO_2^*	PbO_2^*
0.01	51.6	52.2	85.8	87.0	100
0.03	63.3	49.2	64.0	84.5	86.6
0.05	69.4	40.9	53.8	83.7	86.0
0.07	69.0	43.3	44.6	79.9	87.9
0.1	77.5	42.7	28.2	82.1	86.6

$[H_2O_2]$ M	t (40°C)			
	$CuCO_3^*$	Cu^*	Cu	MnO_2^*
0.01	44.1	69.9	100	100
0.03	38.7	63.9	96.8	93.9
0.05	17.7	62.3	95.6	92.9
0.07	15.5	55.3	96.2	93.7
0.1	12.4	42.8	89.4	90.3

$[H_2O_2]$ M	t (60°C)			t (80°C)
	Cu^*	Cu	MnO_2^*	Cu
0.01	92.1	100	100	100
0.03	87.5	100	100	100
0.05	72.4	100	97.2	100
0.07	63.8	99.2	97.4	100
0.1	57.3	97.7	96.8	100

(*)Inmobilized on polyester resin.

obtained with the manifold in which the set column-debubbler was suppressed. Obtained results; mean absorbance values of teen replicates, were as following: a) 0.740; b) 1.110 with and without the corresponding set, respectively. Reproducibility was tested by injecting iproniazide solutions; 3, 5, 7 and 10 mg l^{-1}. The iproniazide is oxidized by the hydrogen peroxyde and monitored fluorimetrically at 320 and 395 nm for excitation and emission, respectively. Four different columns were tested (five replicates each concentration and calculated the line slope; the relative standard deviation of the four slopes was 1.86%.

4. Conclusions

The paper describes the use of H_2O_2 as a reagent (the excess is destroyed) in a FI- assembly with a solid-phase reactor. The effective behaviour of the bed reactor by removing H_2O_2 would let to use it coupled with any kind of detector, even UV-spectrophotometric detection avoiding the strong absorbance of the oxidant in this spectral region.

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