ESTIMATION OF BISMUTH AND MOLYBDENUM IN CATALYST SAMPLES POLAROGRAPHICALLY

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Bismuth molybdate is an important oxidation catalyst used in the production of acrolein and acrylo nitrile. Bismuth and molybdenum in these catalysts are usually determined by EDTA, gravimetric or spectrophotometric methods [1], each component being analysed separately. Even though polarographic methods [2,3] for bismuth and molybdenum are known, estimation of both in a single aliquot is not reported. A simple and faster method for simultaneous estimation of bismuth and molybdenum in a single experiment is reported in this communication.

EXPERIMENTAL

Apparatus

Polaritor Type PO 4 G (Radiometer, Denmark) was used for all experiments. The height of mercury was 51 cm and the drop time was 3.4 seconds. Unless otherwise stated the sensitivity was 20 μa full scale and the chart speed was 2 cm/min.

Reagents

All reagents used were of analytical grade. Double distilled water was used for preparation of solutions.

(a) Bismuth solutions: Bismth metal powder (1.5 g) was dissolved in 10 ml of 14 M nitric acid in a 250 ml beaker. Then 50 ml of water was added and kept on a water bath (70°C). Air was bubbled through the solution while on water bath for 30 min. After cooling, the solution was made up to 250 ml in a volumetric flask. Bismuth was estimated by EDTA using xylenol orange as indicator.

(b) Molybdenum solution: Molybdenum metal powder (1.5 g) was weighed into a 250 ml beaker. Twenty ml of 14 M nitric acid followed by 10 ml of 12 M hydrochloric acid were added and warmed on a water bath (70°C) till all the metal dissolved. While on water bath the mixture was diluted with 50 ml of water and air was bubbled for 30 min. After cooling, the solution was made upto 250 ml in a volumetric flask with water. Molybdenum was estimated gravimetrically as oxinate.

(c) Bismuth molybdate solution: Bismuth molybdate catalyst sample (1.5g) was weighed on to a 25 ml beaker and dissolved as described for molybdenum. Bismuth was determined by EDTA and molybdenum by oxinate methods.

(d) Ammonia-ammonium chloride solution: The solution prepared was 0.2 M in ammonia and 2 M in ammonium chloride.

(e)Tartaric acid: The solution prepared was 1.33 M or about 20% by weight.

Preparation of solutions for polarography

Stock solutions of bismuth, molybdenum and bismuth molybdate were diluted to a metal concentration in the range 10^{-3} -10^{-4} M. Each solution (50 ml) prepared for polarography contained 25 ml of ammonia-ammonium chloride solution, 5 ml of tartaric acid and the requisite concentration of bismuth and molybdenum. The pH was adjusted to 1.9 - 2.2 with hydrochloric acid (1 M) or ammonia (1M) solutions. Pure hydrogen gas was bubbled for 5-10 min at the rate of 200 ml/min. Solutions were polarographed in a 50 ml cell.

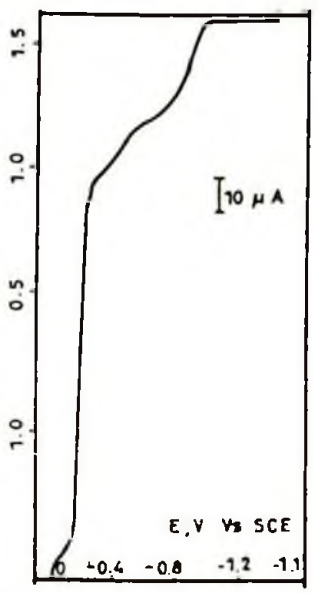


Fig. 1 Polarogram of a mixture of bismuth and molybdenum in an electrolyte consisting of tartaric acid and ammonia-ammonium chloride solution. pH = 2.0, Hg height = 51cm Drop-time = 3.4 sec.

RESULTS AND DISCUSSION

Typical polarogram of bismuth - molybdenum system is shown in fig. 1

In the presence of ammonia-ammonium chloride and tartaric acid electrolyte at pH = 1.9 - 2.2 the polarogrphic wave of bismuth is obtained at -0.1 V and the wave height is linear with concentration in the range 10^{-3} -10^{-4} M. The two polarographic waves of molybdenum are obtained at -0.22 V and at -0.51 V, the former is small and ill defined whereas, the latter wave is distinct and the wave height is proportional to concentration in the range 10^{-3} - 10^{-4} M. Under the experimental con-

TABLE 1

ANALYSIS OF SYNTHETIC MIXTURES OF BISMUTH AND MOLYBDENUM

Sample No.	Bi x 10^{-4} M			Mo x 10^{-4} M		
	Taken	Found	% Error	Taken	Found	%Error
1.	9.57	10.20	6.6	10.42	11.88	14.0 *
2.	8.61	8.52	1.1	10.42	11.36	9.0
3.	7.66	7.46	2.5	10.42	11.36	9.0
4.	6.70	6.50	3.0	10.42	11.36	9.0
5.	5.74	5.51	4.0	10.42	10.94	4.8
6.	4.78	4.78	Nil	10.42	10.74	3.1
7.	3.83	3.64	5.2	10.42	10.74	3.1
8.	2.87	2.68	6.6	10.42	10.02	3.8
9.	1.91	1.87	2.1	10.42	9.80	6.0
10.	0.96	0.92	4.2	10.42	9.80	6.0
11.	4.78	4.69	1.9	20.80	22.80	13.5*
12.	4.78	4.69	1.9	18.76	19.28	2.8
13.	4.78	4.88	2.1	16.68	17.72	6.2
14.	4.79	4.69	1.9	14.60	15.00	2.7
15.	4.78	5.02	0.9	12.51	13.13	5.0
16.	4.78	4.69	1.9	10.42	10.94	5.0
17.	4.78	4.59	4.0	8.34	8.76	5.0
18.	4.78	4.59	4.0	6.25	6.62	5.9
19.	4.78	4.78	Nil	4.17	4.69	12.5*
20.	4.78	4.69	1.9	2.09	2.40	14.8*

* Molybdenum shows high result when concentration is too high or too low in the prescribed range

TABLE 2

ANALYSIS OF BISMUTH MOLYBDATE CATALYST

Sample No.	Bismuth			Error %	Molybdenum			Error %
	Taken mg/ml	Found mg/ml	σ		Taken mg/ml	Found mg/ml	σ	
1.	1.120	1.104	0.022	1.4	0.550	0.555	0.068	0.9
2.	1.360	1.374	0.006	1.0	0.342	0.395	0.041	2.0
3.	1.063	1.103	0.034	3.4	0.500	0.498	0.021	0.4
4.	0.933	0.906	0.025	2.9	0.680	0.670	0.040	1.5

Standard deviation

ditions described above no polarographic maxima were observed and the use of any suppressor adversely affects the molybdenum wave.

Polarograms were recorded for (a) bismuth, (b) molybdenum, (c) synthetic mixtures of bismuth and molybdenum and (d) bismuth molybdate catalyst solutions. Synthetic mixtures were prepared by keeping the concentration of one constituent fixed and varying the other in order to select a range where both elements can be estimated simultaneously within acceptable range of experimental error. The results for bismuth - molybdenum synthetic

TABLE 3

INTERFERENCE OF ADDED METAL IONS IN THE POLAROGRAPHIC ESTIMATION OF BISMUTH AND MOLYBDENUM

Added ion	Effect on bismuth wave	Effect on Molybdenum wave
Co (II), Cu (II), Ni (II), Zn (II)		
Mn (II)	Nil	Nil
Pb (II)	Nil	Yes
Cr (III), Al (III)		
V (V)	Nil	Yes
V (IV)	Yes	Yes
U (VI)	Nil	Yes
Fe (III)	Nil	Yes
Fe (II)	Yes	Yes
Ba (II), Sr (II), Ca (II)	Nil	Nil

mixtures are presented in Table 1. In the case of bismuth molybdate catalysts four samples were polarographed. Average of 8 results were compared with average of corresponding number of classical analysis results. Percentage error and standard deviation[3] corresponding to spread out of errors were calculated and presented in Table 2. The interferences of number of possible promoters and additives were studied and the results are shown in Table 3.

It is seen from the results that bismuth and molybdenum can be determined simultaneously by polarography.

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