

ELIMINATION OF SYSTEMATIC ERRORS DUE TO ADSORPTION IN THE DETERMINATION OF TRACE AMOUNTS OF BISMUTH BY DIFFERENTIAL PULSE POLAROGRAPHY

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The authors were concerned with the adsorption of bismuth ions on the surface of calibrated glass bottles during preparation of standard solutions and on the walls of the polarographic cell during analysis by differential pulse polarography. The adsorption can be prevented by treating the laboratory glass by a solution of O,N-bis-trimethylsilyl-trifluoroacetamide before use. The treatment must be repeated from time to time since its effect weakens by repeated rinsing of the glass.

Problems related with the determination of trace amounts of inorganic compounds and methods of their solution were the subject of many studies^{1,2}. One of the effects that adversely affect the correctness of analytical results is adsorption on the surface of laboratory vessels, especially when these are made of glass³⁻⁵. Since the adsorption depends on the kind of ions and on the working conditions, it must be determined for every particular case separately.

We determined trace impurities in chemicals by differential pulse polarography, which appears suitable for this case^{6,7}. In preparing standard solutions of bismuth, we found that the calibration curves are subject to marked errors due to adsorption of Bi ions on the walls of glass calibrated flasks and polarographic cell. These effects and the way of their elimination are described below.

EXPERIMENTAL

We used a differential pulse polarograph PA 3 (Laboratorní přístroje, Prague) for the determination of Bi ions in the concentration range 0.05–1 µg Bi per 5 ml of supporting electrolyte; the drop time was 2 s, scan rate 5 mV s⁻¹, sensitivity of apparatus 17, modulation 50 mV.

The base electrolyte was 0.2 cm³ of 1M tartaric acid + 0.2 cm³ of 0.8M NaOH + 4.6 cm³ H₂O; its pH was 3.2. The half-wave potential of bismuth was -0.145 V (SCE).

We found that traces of metal ions (Fe, Zn, Ni) could be removed from the base electrolyte solution by two-fold filtration through a paper filter with blue stripe. Its ion-exchange properties were proved by polarographic analysis of the base electrolyte before and after filtration.

Distilled water for preparation of solutions was purified by repeated distillation from a quartz glass bottle with addition of hydrogen peroxide and barium peroxide.

RESULTS AND DISCUSSION

The dependence of the polarographic wave of bismuth ions on their concentration is linear from $0.03 \mu\text{g cm}^{-3}$. At lower concentrations, the dependence is curved owing to the background. The detection limit is $0.01 \mu\text{g cm}^{-3}$, below which the polarographic wave is masked by the noise.

The linear dependence, of course, does not mean that the measured results are correct. To check the influence of some factors, mainly adsorption, on their correctness, we prepared three solutions containing 10, 5, and $1 \mu\text{g}$ of Bi in 1 ml by dilution of a stock solution containing 1 mg Bi per 1 ml, whose required volume was placed in a calibrated flask and made up to the mark with the base electrolyte. Of these solutions, we took such quantities as to obtain the same concentration of bismuth ions in the polarographic cell. The most concentrated solution was pipetted by means of a microsyringe (Hamilton). The polarographic wave was expected to be the same in height in all cases.

The mean value from three measurements was taken and the results were evaluated. Although the concentration dependences were linear in all the three cases, their slopes were not equal. The mean wave heights are given in Table I. It follows from these data that the dilution of the solution in a volumetric flask causes a decrease in the concentration of bismuth as a result of adsorption on the glass-electrolyte interface. If the polarographic wave heights of the solutions prepared from the solution of $10 \mu\text{g}$ of Bi per 1 ml are denoted as 100%, then the same procedure starting from the more dilute solution of $5 \mu\text{g}$ of Bi per 1 ml gave results lower by 8.2%. In the third case, starting from the solution of $1 \mu\text{g}$ Bi per 1 ml, the wave heights were by about 10% lower than in the second.

TABLE I

Relative decrease of the polarographic wave height of bismuth ions caused by adsorption on the volumetric flask. The per cent wave height in column B is referred to A, in C to B (in parentheses)

Bi conc. g ml^{-1}	Wave heights for starting Bi solutions:		
	10 mg ml^{-1} (A) mm (%)	5 mg ml^{-1} (B) mm (%)	1 mg ml^{-1} (C) mm (%)
0.2	42.2 (100)	38.8 (91.9)	31.5 (81.2)
0.4	107.5 (100)	98.7 (91.8)	88.6 (89.7)
0.6	172.8 (100)	158.6 (91.8)	145.7 (91.8)
0.8	238.1 (100)	218.5 (91.8)	202.8 (92.8)
1.0	303.4 (100)	278.4 (91.8)	259.4 (93.1)

In the reverse case, when a solution of lower concentration was poured into a calibrated flask which had contained before a solution of higher concentration and which had been rinsed out with water, the polarographic wave was somewhat higher.

The adsorption of bismuth took place also in the polarographic cell. For example, we poured 5 ml of a solution containing 0.1 μg of Bi into the thoroughly cleaned polarographic cell and measured the wave height. The experiment was repeated four times and the results were as follows:

No of experiment	1	2	3	4
Wave height, mm	12	50	56	57

These results indicate that an adsorption equilibrium was reached after the fourth filling of the cell.

Thus, it is obvious that adsorption of bismuth ions must be prevented in order to obtain reliable analytical results. This can be achieved by silylation of the siloxane groups of the glass surface. We used O,N-bis-trimethylsilyl-trifluoroacetamide (Merck, Darmstadt).

The procedure of silylation was as follows. The laboratory flasks were rinsed with redistilled water, filled with 50% HNO_3 and allowed to stand overnight. Afterwards they were rinsed several times with water, dried, filled with 2 ml of the silylation agent so as to wet completely the glass surface, closed, and put into a thermostat at 50°C. After 30 min the silylation agent was poured out and the flasks were rinsed with redistilled water. The polarographic cell and the capillary were treated in the same way.

By using the silylated calibrated flasks and polarographic cell, we obtained polarographic waves of bismuth ions whose heights were not affected by adsorption and were linearly dependent on the concentration of bismuth ions. Further we prepared several solutions containing 1 μg of Bi in 25 ml volumetric flasks; the pipetted volumes were made up to the mark with the base electrolyte. The measured wave heights (mean values from three measurements) obtained with these solutions are as follows:

Starting Bi conc., $\mu\text{g cm}^{-3}$	0.04	0.10	0.20	0.40	0.80	1.00
Pipetted volume, ml	25	10	5	2.5	1.25	1.00
Wave height, mm	184	187	188	192	187	186

Also these data indicate that adsorption of bismuth ions was prevented by silylation of the laboratory glass.

Thus, if the H atom of the siloxane group, which functions as ion exchanger, is replaced by the hydrophobic trimethylsilyl group, errors due to adsorption on the glass-solution interface can be prevented. The treatment has a favourable effect on the polarographic capillary. If the analysed solution penetrates into an ordinary

polarographic capillary, the capillary must be cleaned thoroughly for a long time, whereas a silylated capillary needs only be rinsed with distilled water. A disadvantage of the proposed treatment is that it is not very durable: after repeated contact with electrolyte solutions, the silylation must be renewed.

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