Colloidal precipitation floatation of bismuth

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A method is described for complete separation of bismuth(III) from aqueous solutions as colloidal sulphide precipitate using sodium sulphide as a precipitant and oleic acid as a surfactant. Hydrogen ion concentration appears to be an important factor affecting the floatation process. At pH 1.0 bismuth(III) was completely floated. The floatation of bismuth(III) was successful in the presence of some foreign ions. It was found that, the order of the additive additive reagents and the temperature markedly affect the floatability. Moreover, ionic strength has no appreciable effect on the floatation efficiency. A suggested mechanism for the floatation process has been proposed.

Although collection of traces of various metal ions on inorganic or organic precipitates offers a useful separation technique in trace analysis and radiochemistry. Difficulties, however, sometimes arise in separating the precipitate from the mother liquor. The colloidal precipitate formed by adding sodium sulphide solution to an aqueous acidic solution is a good collector for bismuth, but cannot be filtered off easily; it clogs the pores of some filters and passes through the others. Numerous techniques exist to remove metal ions from aqueous solutions. Of these, the floatation separation technique has been of considerable interest in recent years.

Bismuth and its compounds have been used in different types of chronic constipation drugs. It is a geochemically important metal used in synthesizing metal-based alloys. It is also an interesting trace element, which presents a potential public health problem. Therefore, considerable attention has been devoted to trace preconcentration and determination of bismuth in several drugs, metal-based alloys and rocks by various techniques.

The majority of papers dealing with preconcentration of bismuth are focussed on ion exchange, solvent extraction and floatation techniques. Some workers have floated bismuth after coprecipitation on Fe(OH)₃ or PbSO₄. Therefore, it was the purpose of this investigation to reduce floatation steps using a common reagent.

Experimental Procedure
The floatation cell was a test tube of 12 mm inner diameter and 290 mm long with a stopcock at the bottom. All glassware were soaked overnight in 50% nitric acid and rinsed thoroughly before use with double distilled water. The pH measurements were carried out with HANNA Instruments 8519, Digital pH-meter. Griffin Colorimeter, Model 40, was used throughout.

Unless otherwise stated, all the reagents were of Analar and BDH grades. The aqueous solutions were prepared in double distilled water. Bismuth standard solution (1 mg/mL) provided by BDH Laboratory Chemicals for atomic absorption spectroscopy. Sodium sulphide stock solution (0.1 mol L⁻¹). 9.6 g of Na₂S.9H₂O were dissolved in one litre of water. Oleic acid (HOL) stock solution (6.36 × 10⁻² mol L⁻¹). 20 mL of HOL, food grade (d 0.895) were dispersed in one litre of kerosene. Thiourea (Tu) stock solution (0.5 mol L⁻¹), 38.6 g were dissolved in one litre of water.

Floatation procedure—To carry out the floatation measurements, 20 cm³ of an aqueous solution containing bismuth ions, sodium sulphide, oleic acid surfactant and HNO₃ or NaOH, for controlling the pH, was introduced into the floatation cell. The floatation cell was turned upside down repeatedly twenty times by hand. Concentration of Bi³⁺ ions in the underlying solution was determined colorimetrically. The floatability (F%) was calculated by the following equation:

\[ F = \frac{C_i - C_f}{C_i} \times 100\% \]

where \( C_i \) and \( C_f \) denote the concentration of Bi³⁺ ions before and after floatation, respectively.
To study the effect of temperature, the Bi$^{3+}$ solution, the surfactant and sodium sulphide solution were either heated or cooled to the same temperature. The sodium sulphide and HOL were quickly poured into the Bi$^{3+}$ solution at a time zero. The solution was introduced into the floatation test tube, jacketed with 1 cm thick fibre glass insulation. The same procedure of floatation mentioned above was followed. Most of the floatation occurred in the first few minutes and the fact that the test tube was not thermostated (but only insulated) and the small changes in the floated solution temperature occurred after 12 min should have had a minimal effect on the floatation response.

Other measurements were carried out at room temperature, e.g., ~25°C. Each point in the results is the average of three experiments.

**Results and Discussion**

Preliminary tests were carried out to select the suitable concentration of HOL, which gives the maximum floatation of bismuth. It has been found that, $4.77 \times 10^{-3}$ mol L$^{-1}$, is the suitable concentration of HOL. So, such HOL concentration has been used throughout the study.

**Effect of Bi(III) concentration**—Data in Fig. 1 show the floatability of different concentrations of Bi$^{3+}$ ions using $4.77 \times 10^{-3}$ mol L$^{-1}$ HOL at pH 1 without (curve ●) and with (curve ○) the addition of sodium sulphide. The effect of addition of $75 \times 10^{-5}$ mol L$^{-1}$ sodium sulphide is evident from comparing the two curves in Fig. 1. It has been found that the floatability of bismuth ions does not exceed 63%, whereas, it reaches 100% in the presence of sodium sulphide. At higher concentration of bismuth the floatation efficiency decreases because of the absence of enough sodium sulphide precipitant.

**Effect of sodium sulphide concentration**—Fig. 2 presents, the effect of sodium sulphide on the floatability of 15 ppm bismuth at HOL concentration ($4.77 \times 10^{-3}$ mol L$^{-1}$) and pH 1. As may be seen, a floatation of nearly 100% is obtained at $75 \times 10^{-5}$ mol L$^{-1}$ of sodium sulphide concentration level and the curve gives plateau. During our experiments the concentration of sodium sulphide is fixed at such level.

**Effect of hydrogen ion concentration**—It was attempted to study the effect of pH on the floatation of 15 ppm bismuth from aqueous solutions in the presence of HOL and Na$_2$S. The results are shown in Fig. 3. It is evident that, colloidal bismuth sulphide has been completely floated at

![Graph](image-url)

**Fig. 1**—Floatability of different concentrations of Bi$^{3+}$ at HOL ($4.77 \times 10^{-3}$ mol L$^{-1}$) and pH = 1 [● Without Na$_2$S; ○ With Na$_2$S ($75 \times 10^{-5}$ mol L$^{-1}$)]

**Fig. 2**—Effect of Na$_2$S concentration on the floatability of Bi$^{3+}$ (15 ppm) at HOL concentration ($4.77 \times 10^{-3}$ mol L$^{-1}$) and pH = 1

**Fig. 3**—Effect of pH on the floatability of Bi$^{3+}$ (15 ppm) with Na$_2$S ($75 \times 10^{-5}$ mol L$^{-1}$) and HOL ($4.77 \times 10^{-3}$ mol L$^{-1}$)
pH ≤ 1.5. At pH 2 or more, the flotation decreases under 80% level. Such depression in flotation efficiency, may be attributed to the hydrolysis of Bi(III) salts in aqueous solutions at pH 2 or more to precipitate basic salts. Above pH 10, more depressive flotation has been obtained due to the formation of white precipitate and excessive foams from the HOL surfactant.

Effect of foreign ions—A series of experiments were conducted to study the floatation of Bi(III) from aqueous solutions containing some ions (Pb, Cu, Hg, Cd, Mn, Zn, Co, Ni, As and Sb, up to 1 mg/mL concentration level), each individually or in combination. This addition had no effect on floatation percentage especially in the presence of sufficient amount of sulphide ions.

Order of additives—The order of adding reagents markedly affects the floatation of Bi(III) ions. The addition of the reagents in the order: bismuth ions + sulphide solution + HOL surfactant is the optimal sequence. Addition of the sulphide as the last reagent results in a white precipitate, foaming and dispersion of the HOL surfactant with very low flotation of Bi³⁺ ions. This may due to an interaction between sulphide ions and HOL surfactant.

Effect of ionic strength—A series of experiments were carried out to study the effect of ionic strength on the floatation efficiency of Bi³⁺ ions with HOL surfactant in the presence of Na₂S. The test solutions were KCl, NaCl, NaNO₃ and CaSO₄. All the studied compounds have no effect on floatability of bismuth at different conditions. However, CaSO₄ decreases slightly the floatation efficiency of Bi³⁺ ions which may be due to the formation of insoluble calcium oleate and to further modifications in surface area of the precipitate.

Floatation mechanism—Colloidal systems are characterised by the presence of polar points on their surfaces originating from the solvation of countereions of the electrical double layer. Moreover, oleic acid—which may have a polar point on its carboxylic group, interacts electrostatically with the colloidal sulphide precipitate giving the sublate which may be floated by air bubbles in the solution (Fig. 4).

References
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