Detection, Quantitative Collection and Semiquantitative Determination of Bismuth(III) and Zinc(II) in Aqueous Media Using Polyurethane Foam Treated with Dithizone

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The analytical utility of dithizone foam for the detection, quantitative collection and semiquantitative determination of traces of bismuth and zinc in aqueous solutions has been examined. The effect of pH on the sensitivity and selectivity of the proposed foam tests has been investigated. The detection limits of bismuth and zinc by the foam batch method are 0.02 and 0.003 ppm, respectively. The effect of diverse ions on the detection of bismuth and zinc has been critically investigated. A quantitative collection of bismuth and zinc from extremely dilute aqueous acidic solutions by the proposed foam column method has been successfully carried out.

Keywords Polyurethane foam test, dithizone, extraction, bismuth, zinc, qualitative inorganic analysis, semiquantitative inorganic analysis

Diphenylthiocarbazone (dithizone) is an extremely sensitive reagent that can be used for the extraction and determination of microgram quantities of many metal ions.¹⁻³ Metal dithizonate complexes are easily extracted with various organic solvents. It is known that dithizone is not a selective reagent in neutral and alkaline media. However, its selectivity is generally increased at lower pH values and by adding a complex forming agent or masking agent to the aqueous solution.⁴

Polyurethane foams loaded with dithizone have been employed for the quantitative collection and preconcentration of mercury⁵, silver⁶ and other metal ions from their dilute aqueous solutions. Foams loaded with other organic reagents (Chromofoams) have been suggested⁷⁻¹³ for the sensitive detection and semiquantitative determination of several metals.

No work has been done on the application of dithizone loaded foam for the detection, collection and preconcentration of bismuth(III) and zinc(II) in aqueous media. The only work reported¹⁴ regarding the detection of zinc with dithizone foam was carried out in a neutral medium in which the reagent foam is not selective. Accordingly, this paper describes the use of dithizone foam for the selective detection, quantitative collection and semiquantitative determination of traces of bismuth and zinc in aqueous acidic solutions.

Experimental

Reagents and materials

All reagents were of analytical-grade unless otherwise

specified. An open-cell polyether type polyurethane foam (bulk density 30 kg m⁻³) was supplied by K. G. Greiner, Schaumstoffwerk-Kremünster, Austria. The foam material (cubes of ca. 5 mm edge) was washed and dried as previously described.¹⁴ Stock solutions containing 1 mg ml⁻¹ of bismuth and zinc were prepared by dissolving the appropriate amounts of bismuth(III) nitrate and zinc(II) sulfate in deionized water acidified with a few drops of 1 M nitric acid solution and standardized by EDTA titration. Series of standard bismuth and zinc solutions were prepared by dilution with water acidified with a few drops of 1 M nitric acid solution.

The dithizone solution was prepared by dissolving 0.05 g of dithizone in 100 ml of chloroform. The reagent foam was prepared by mixing the dried foam cubes and the dithizone solution (5 ml g⁻¹ dry foam) with efficient stirring for 5 min. The dithizone-loaded foam material was then squeezed between two watch glasses to remove any excess of dithizone solution.

A foam column was prepared by packing 1 g of the reagent foam cubes in a glass column (1 cm diameter and 15 cm long) filled with sufficient water to immerse the foam material. Air bubbles in the foam bed were removed by compressing the cubes several times with a glass rod.

In batch (static) experiments, one dithizone-loaded foam cubes is mixed and shaken with 1–3 ml of the test solution for 2–3 min. A color change of the foam from green to orange-brown or pink, in the presence of bismuth and zinc, respectively, was observed. For a semiquantitative determination of bismuth and zinc,

standard color scales were prepared with a series of standard solutions of different concentrations of each metal ion. The concentration of the unknown sample was determined by a comparison.

In the column (dynamic) experiment 10, 100 and 250 ml of the test solution were allowed to percolate through the foam column at flow rates of 0.5–1.0 and 3–5 ml min⁻¹ with bismuth and zinc solutions, respectively.

Instrumentation

Atomic absorption measurements were carried out using a Perkin Elmer graphite furnace atomic absorption spectrophotometer, Model AA 5000.

Results and Discussion

Determination of bismuth with dithizone foam

Dithizone forms an insoluble orange-brown color complex with bismuth(III) (Bi(HDz)₃) that is readily extracted by organic solvents without any color change.⁴ This reaction was tried with foam loaded with dithizone to detect bismuth in acidic aqueous solutions (pH≈1.2). At this pH, the complexation reaction is quite selective for bismuth. Since the primary bismuth

dithizonate complex collected on the relatively high available surface area of the foam cube is quite stable and the characteristic color can easily be observed on the foam, it was possible to detect bismuth at a concentration as low as 0.02 ppm (μg ml⁻¹) using the foam batch extraction mode.

To examine the selectivity of this dithizone foam test, the detection of bismuth in the presence of diverse types of ions was studied using a straight-forward foam batch method. It was found possible to detect 1 μg of bismuth in the presence of up to 10 mg of Ca²⁺, Ba²⁺, Mg²⁺, Mn²⁺, Pb²⁺, Co²⁺, Tl⁺, Zn²⁺, Cl⁻, Br⁻, F⁻, SO₃²⁻, BrO₃⁻, ClO₃⁻, ClO₄⁻, SeO₃²⁻, S₂O₅²⁻, acetate, thiourea, ascorbate, tartrate, citrate and phosphate. In the presence of some other ions, a simple modification of the sample solution afforded unambiguous and sensitive detection of bismuth (Table 1).

A semiquantitative determination of bismuth was possible by a comparison of the color of the foam cube with standards prepared with 0.02, 0.1, 0.5, 1.0 and 20 ppm bismuth solutions under the same experimental conditions. Bismuth at lower concentrations (≤0.01 ppm) can be detected by passing 10 ml or more of bismuth solution through the reagent foam column at a rate of 0.5–1.0 ml min⁻¹. The length of the colored zone is proportional to the bismuth concentration, which could be estimated using standards covering the range of 0.01 to 5 μg ml⁻¹. Figure 1 shows, *e.g.*, the relationship between the bismuth concentration in 10 ml aqueous solution and the length of the colored zone on the foam column. Similar linear relationships were also obtained with 100 and 250 ml bismuth solutions.

It is worth to mention that, the length of the colored zone is not affected by dilution, *i.e.*, 1 μg of bismuth in 10, 100 or 250 ml of aqueous solution (pH≈1.2) gave more or less the same length of the colored zone on the dithizone foam columns. That is, foam visual colorimetry could be successfully employed for a semiquantitative determination of bismuth in an extremely dilute aqueous solution.

Table 1 Detection of bismuth(III) with dithizone foam in the presence of some interfering ions

Foreign ion	Compound added	Tolerance limit	Note
Sr ²⁺	SrCl ₂ ·6H ₂ O	1:1×10 ³	
Ni ²⁺	NiSO ₄ ·6H ₂ O	1:1×10 ³	
Zr ⁴⁺	ZrOCl ₂ ·8H ₂ O	1:1×10 ³	
Au ³⁺	AuCl ₃	1:1×10 ³	
Hg ²⁺	Hg(NO ₃) ₂ ·H ₂ O	1:1×10 ³	Add 0.5 ml of a saturated ascorbic acid solution.
Cd ²⁺	Cd(NO ₃) ₂ ·4H ₂ O	1:1×10 ⁴	Add a few crystals of Na ₂ SO ₃ .
Cu ²⁺	CuSO ₄ ·5H ₂ O	1:1×10 ⁴	Adjust the pH of the aqueous soln. to ≈0.8.
Fe ³⁺	FeCl ₃ ·6H ₂ O	1:1×10 ⁴	Add a few crystals of NaF.
Ag ⁺	AgNO ₃	1:1×10 ⁴	Add a few crystals of KSCN or thiourea.
S ₂ O ₈ ²⁻	K ₂ S ₂ O ₈	1:1×10 ³	
VO ₃ ⁻	NH ₄ VO ₃	1:1×10 ³	
WO ₄ ⁻	Na ₂ WO ₄ ·2H ₂ O	1:1×10 ³	
Oxalate	sodium oxalate	1:1×10 ³	Add bromine water and boil.
MnO ₄ ⁻	KMnO ₄	1:1×10 ⁴	Add a few crystals of Na ₂ S ₂ O ₃ .
S ₂ O ₃ ²⁻	Na ₂ S ₂ O ₃ ·5H ₂ O	1:1×10 ⁴	Add bromine water and boil.
I ⁻	KI	1:1×10 ⁴	Add bromine water and boil.

Fig. 1 Relationship between the bismuth concentration and the length of the colored zone.

An attempt was made for a quantitative collection of bismuth(III) on columns packed with dithizone foam. The foam bed was 9.0 cm in length, and bismuth solutions ($\text{pH} \approx 1.2$) containing $10 \mu\text{g}$ of bismuth in 10, 100 or 250 ml were allowed to pass through the foam columns at a flow rate of $0.5 - 1.0 \text{ ml min}^{-1}$.

Bismuth was determined in the effluent solutions by an atomic absorption spectrophotometric method using a hydride system. The obtained results show that bismuth could be quantitatively collected from these dilute aqueous solutions onto the foam column, since no bismuth could be detected in the effluent solutions.

Determination of zinc with dithizone foam

Dithizone forms a pink colored primary complex with zinc in neutral and slightly alkaline media.⁴ This reagent has been employed for the preconcentration and quantitative determination of zinc in liquid-liquid extraction systems. Carbon tetrachloride and chloroform were employed as solvents with aqueous zinc solutions at pHs 6–9.5 and 7–10, respectively. Hydrophobic gel impregnated with dithizone has been used for the collection of zinc in aqueous solution employing column extraction system at pHs 4–7. Polyurethane foam loaded with dithizone has been suggested¹⁴ for the detection and semiquantitative determination of zinc in aqueous solution at pH 6.2. Unfortunately, however, this method is not selective for zinc since at this relatively high pH many other heavy metals react with dithizone while producing different colored complexes.⁴

In batch extraction experiments the effect of the pH of the aqueous solution on the extraction of zinc with dithizone foam has been critically evaluated. During this study a few drops of a saturated sodium sulfite solution was added in a trial to prevent the oxidation of the reagent to diphenylthiocarbazone ($\text{S}=\text{C}(\text{N}=\text{NC}_6\text{H}_5)_2$) which does not react with zinc.

In the absence of sulfite ion the suitable pH for the extraction of zinc with dithizone foam was found to be in the range 4.5 to 6.5. Surprisingly, however, in the presence of sulfite ion in aqueous solution, zinc was extracted and the pink colored complex of zinc was clearly observed on the reagent foam material at lower pHs (nearly 1.8). Thus, solutions having pHs ranging between 1.8 and 6.5 are quite suitable for the extraction of zinc with the proposed dithizone foam in the presence of sulfite ion. Moreover, the color of the zinc complex seems to be more intense in the presence of sulfite ions which allow the detection of as low as 0.003 ppm of zinc. Figure 2 shows the effect of the pH of an aqueous solution in the presence of sodium sulfite on the collection of zinc with dithizone foam in batch extraction experiments. Zinc remaining in the aqueous phase was measured by an atomic absorption spectrophotometric method and the percentage of zinc retained on the reagent foam was calculated in terms of the difference.

Most probably, sulfite ion participates in a mixed coordination sphere, i.e., a triple complex¹⁵, may be

Fig. 2 Effect of the pH of the aqueous solution on the extraction of zinc with dithizone foam. Concentration of Zn^{2+} : $1 \mu\text{g}/3 \text{ ml}$ aqueous solution containing 1% sodium sulfite; shaking time: 3 min with one reagent foam cube.

formed, since the pink color of the zinc dithizonate complex is more clearly observed and is also more stable.

At this stage, this finding was applied to the detection and semiquantitative determination of zinc using dithizone foam cubes at pH 1.8. The proposed method was found to be quite selective. At this pH value the effect of different ions (previously mentioned during testing of the selectivity of dithizone foam for the extraction of bismuth) were found to have no effect on the detection of zinc with dithizone foam. Interference due to the presence of the ions listed in Table 1 are eliminated in a similar way as in the case of bismuth. The only interference was observed in the presence of mercury, silver, copper or bismuth together with zinc in an aqueous media. However, this interference could be successfully eliminated by the addition of a few crystals of sodium thiosulfate, which prevent the reaction of these metal ions with dithizone foam.

A semiquantitative determination of zinc in a foam batch extraction system was also possible using a standard color scale covering the concentration range of 0.003 to 5 ppm.

A further important advantage of the proposed reagent foam is the possibility of using it for a semiquantitative determination and a quantitative collection of zinc from an extremely dilute acidic aqueous solution employing a foam column extraction technique in a way similar to that described regarding bismuth. A flow rate of $3 - 5 \text{ ml min}^{-1}$ was found to be suitable for this purpose.

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