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Extraction, Separation, and Determination of Nickel and Bismuth with1-(2-Pyridylazo)-2-naphthol in Aqueous Thiocyanate Media

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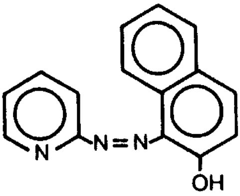
ABSTRACT

Nickel(II) and bismuth(III) are quantitatively extracted from aqueous thiocyanate solutions, adjusted to pH 4.0–9.0 and 3.5–5.0, respectively, using solutions of 1-(2-pyridylazo)-2-naphthol (PAN) in tri-*n*-butyl phosphate (TBP). The extracted species of nickel and bismuth have the formulas [Ni(PAN)SCN]·4TBP and [Bi(PAN)SCN]X·TBP, respectively. Polyurethane foam treated with TBP solution containing PAN is used successfully for the quantitative retention and recovery of nickel and bismuth from aqueous thiocyanate solutions in the column extraction mode. The preconcentration of small amounts (10 μg) of nickel and bismuth from dilute aqueous solutions (1 L) is also possible, with a recovery of 95–97%. The feasibility of using PAN–foam for selective detection and semiquantitative determination of nickel and bismuth in aqueous thiocyanate media is examined. The detection limits of nickel and bismuth by the foam batch method are 0.05 and 0.50 ppm, respectively. Lower concentrations of these metal ions are easily detected in dynamic tests using PAN–foam columns. Semiquantitative determination of nickel and bismuth is also achieved in both the batch and column methods by using the appropriate color scales.

INTRODUCTION

1-(2-Pyridylazo)-2-naphtol (PAN, Formula I) is one of the most widely used 2-pyridylazo compounds in extraction and separation of various metal ions (1–3). In addition to being an excellent metallochromic indicator (1, 4), PAN serves as a chromogenic agent (4, 5) in the determination or detection of over 30 elements. The metal–PAN complexes are practically insoluble in water but are readily soluble in organic solvents. Various elements are extracted over a wide pH range covering mineral acids to alkaline media (6, 7). A chemically modified electrode containing PAN has been suggested recently (8) for the determination of bismuth in aqueous solutions.



Formula I

Since many ions react in a similar way with PAN, such a reaction is not specific for a particular ion. However, its selectivity could be increased by appropriate control of pH and use of masking agents (1–3).

Ion-exchange resins and resilient polyurethane foams have been employed as suitable media (9, 10) for increasing the selectivity and sensitivity of PAN to metal ions. The incorporation of PAN into a resin matrix for producing a chelating ion exchanger and the behavior of the PAN–resins were examined (11, 12). Several metal ions were successfully detected on Dowex 50W-X4 or Dowex 1-X4 with PAN.

Plasticized and unplasticized PAN–polyurethane foams have successfully been used (10) for quantitative separation and rapid collection of some selected metal ions using the batch and column techniques. Polyurethane foam loaded with PAN has also been recommended (13) for the detection and semiquantitative determination of cobalt(II) and mercury(II) in aqueous media.

In this work a detailed study of the quantitative extraction of nickel and bismuth in aqueous thiocyanate media by using liquid–liquid and liquid–solid extraction systems is reported. Sensitive detection and semiquantitative determination of the tested metal ions are shown.

EXPERIMENTAL

Reagents and Materials

Unless otherwise stated, all the reagents were of analytical grade. Tri-*n*-butyl phosphate (TBP) was purified as described by Hamlin et al. (14). An open cell polyether type, flexible polyurethane foam with a bulk density of 30 $kg \cdot m^{-3}$ was supplied by K. G. Greiner, Schaustoffwerk Kremuster, Austria. The foam material (5 mm cubes) was washed and dried as previously described (15). A stock solution of bismuth was prepared by dissolving 0.1 g of 99.9% pure bismuth metal in 5 mL concentrated HNO_3; the acid solution was evaporated to dryness on a steam bath. The residue was then dissolved and diluted with 100 mL of a 0.1 M HNO_3 solution. A stock solution of 1 $mg \cdot mL^{-1}$ nickel was prepared by dissolving the appropriate amount of $NiCl_2$ in deionized water, which was acidified with a few drops of 1 M HNO_3. The resultant nickel and bismuth solutions were standardized by EDTA titration. Two series of standard nickel and bismuth solutions were prepared by diluting the appropriate stock solution with water acidified with a few drops of 1 M HNO_3 solution.

Apparatus

Columns. Glass columns 15 cm long of 5, 10, 15, and 25 mm i.d. were used. A separatory funnel was fitted at the top of the column as a reservoir.

Spectrophotometer. A Perkin-Elmer UV-Visible spectrophotometer Model 552 was employed with a 1-cm quartz cell.

Column Preparation. For quantitative separation purposes, 3 g of the reagent foam cubes were packed in the 15-cm long column of 15 mm i.d. by the vacuum method of foam column packing (10). In the semiquantitative column experiments, 5 mm i.d. columns were packed with 0.7 g of the reagent foam.

Procedure

Foam Batch Tests

In these experiments a PAN–foam cube was shaken with 1–3 mL of the analyte solution in a normal test tube for 1–2 minutes. A color change of the foam was then observed. The color developed in the foam was compared with a standard color series for the semiquantitative determination of nickel and bismuth. For the detection and semiquantitative determination of these elements in more dilute solutions (<0.05 and 0.5 ppm of nickel and bismuth, respectively), the reagent foam cube was shaken with a 25-mL aliquot of the sample in a stoppered flask for 5 minutes.

Foam Column Experiments

Separation of Nickel and Iron. The feed solution contained 2 mL $NiCl_2$ solution (10 $\mu g\ Ni^{2+} \cdot mL^{-1}$), 2 mL $FeCl_3$ solution (10 $\mu g\ Fe^{3+} \cdot mL^{-1}$), 5 mL of 0.5 M KSCN solution, 5 mL of 10% NaF solution, and 4 mL of 1 M $NaNO_3$ solution. This mixture was adjusted to pH 9, and sorption took place at 2–3 $mL \cdot min^{-1}$. Iron was removed with 25 mL of 10% NaF solution. Acetone (50 mL) was then used to recover the nickel–panate complex.

Separation of Nickel or Bismuth and Manganese or Cadmium. A mixture of 2 mL nickel (10 $\mu g \cdot mL^{-1}$) or bismuth (10 $\mu g \cdot mL^{-1}$), 2 mL manganese (10 $\mu g \cdot mL^{-1}$) or cadmium (10 $\mu g \cdot mL^{-1}$), 5 mL of the thiocyanate solution, and 4 mL $NaNO_3$ solution was used as a feed solution. Sorption of this mixture (pH ~ 9) took place at 2–3 $mL \cdot min^{-1}$; a 20-mL thiocyanate solution (0.5 M) was then used for washing the column. Manganese or cadmium was eluted with 50 mL acetate buffer (pH 4.5), and the nickel or bismuth complex was then eluted with acetone (50 mL) at 2–3 $mL \cdot min^{-1}$.

Separation of Nickel, Iron, and Manganese. The feed solution contained 2 mL of each of the nickel, iron, and manganese solutions, 5 mL of 0.5 M thiocyanate solution, and 4 mL of 1 M $NaNO_3$ solution. This mixture was adjusted to pH 9, and iron was removed from the column with 25 mL of 10% NaF solution. Manganese was then eluted with 50 mL of the acetate buffer (pH 4.5), and finally nickel was recovered with 50 mL acetone.

Analytical Methods

All the eluate solutions were evaporated on a steam bath, digested twice with 10 mL portions of a 1:1 mixture of H_2SO_4 and HNO_3, and evaporated with 5 mL HNO_3. Nickel was determined spectrophotometrically as the nickel–dimethylglyoxime complex (2) at 445 nm. Bismuth and cadmium were determined spectrophotometrically by the dithiazone method (2) at 490 and 520 nm, respectively. Iron and manganese were also determined spectrophotometrically by the thiocyanate and permanganate methods (2) at 495 and 528 nm, respectively.

RESULTS AND DISCUSSION

Nickel(II) forms a red complex when reacted with PAN at pH 5–9. This complex is extractable by various organic solvents. The organic extract shows absorbance maxima in the 530–575 nm spectral range. The nickel-to-PAN molar ratio in this extract is 1:2 (1). On the other hand, bismuth forms a pink complex with PAN that is extracted by methyl isobutyl ketone (MIBK) in the presence of an excess of thiocyanate. The bismuth-to-PAN molar ratio is claimed (7) to be 1:1. The bismuth complex shows an absorbance with a maximum at 560 nm.

In the present work the influence of various inorganic and organic anions on the extraction of nickel and bismuth with a solution of PAN in

CCl_4 containing TBP has been examined. A highly significant rise in the extraction efficiency of nickel and bismuth when using this PAN solution is observed in the presence of thiocyanate ion in the aqueous solution.

Liquid–liquid extraction experiments showed that the extraction of nickel and bismuth depends on the shaking time, pH, and thiocyanate concentration in the aqueous phase, and also on TBP and PAN concentrations in the organic phase. For studying the effect of shaking time, fixed concentrations of both TBP (3 M) and PAN (0.002%) in the organic phase (5 mL) and fixed amounts of nickel (5 μg) or bismuth (10 μg), thiocyanate (2.5 mL of 1 M), and $NaNO_3$ (0.5 mL of 5 M) in the aqueous phase (pH ~ 5) were used. A contact time of 5 minutes was found to be more than adequate to attain maximum extraction of the nickel– and bismuth–panate complexes.

The influence of PAN concentration in the organic phase on the extraction efficiency of nickel and bismuth in the presence of $NaNO_3$ was also investigated for PAN concentrations of 1–1000 μM while maintaining the values of all the other parameters. The curves of Fig. 1 show the distribution ratios (*D*) for nickel and bismuth under equilibrium conditions as a function of PAN concentration in the organic phase. The metal-to-PAN molar ratio of the extracted species was calculated by the slope method (10). The results indicate that this ratio is 1:1 for both nickel– and bismuth–panate complexes.

To examine the effect of the pH of the aqueous solution on nickel and bismuth extraction, two series of aqueous solutions (5 mL) were made with a definite amount of nickel (5 μg) or bismuth (10 μg). The pH of these solutions was adjusted to the 2–11 range by using HCl and NaOH. The nickel or bismuth in these solutions was extracted using a 0.08 mM solution of PAN in TBP (2.88 M) with CCl_4 as a diluent; all other parameters were maintained at constant values. The results (Fig. 2) show that 4–9 and 3.5–5 are the optimum pH ranges for nickel and bismuth, respectively. The slopes of log *D* versus pH plots (at a constant PAN concentration) indicate that only one proton of PAN is released on chelation with nickel or bismuth, which is in good agreement with the above results.

In an attempt at establishing the probable composition of the extracted solvated species, the distribution ratios of nickel– and bismuth–PAN complexes were determined at different TBP concentrations using CCl_4 as a diluent. Figure 3 illustrates plots of log *D* versus log TBP concentration for nickel and bismuth. The slopes of these plots indicate the presence of 4 moles of TBP in the extracted species of nickel and only 1 mole for bismuth.

The effect of thiocyanate concentration in the aqueous phase on the extraction of nickel and bismuth complexes is also investigated. The num-

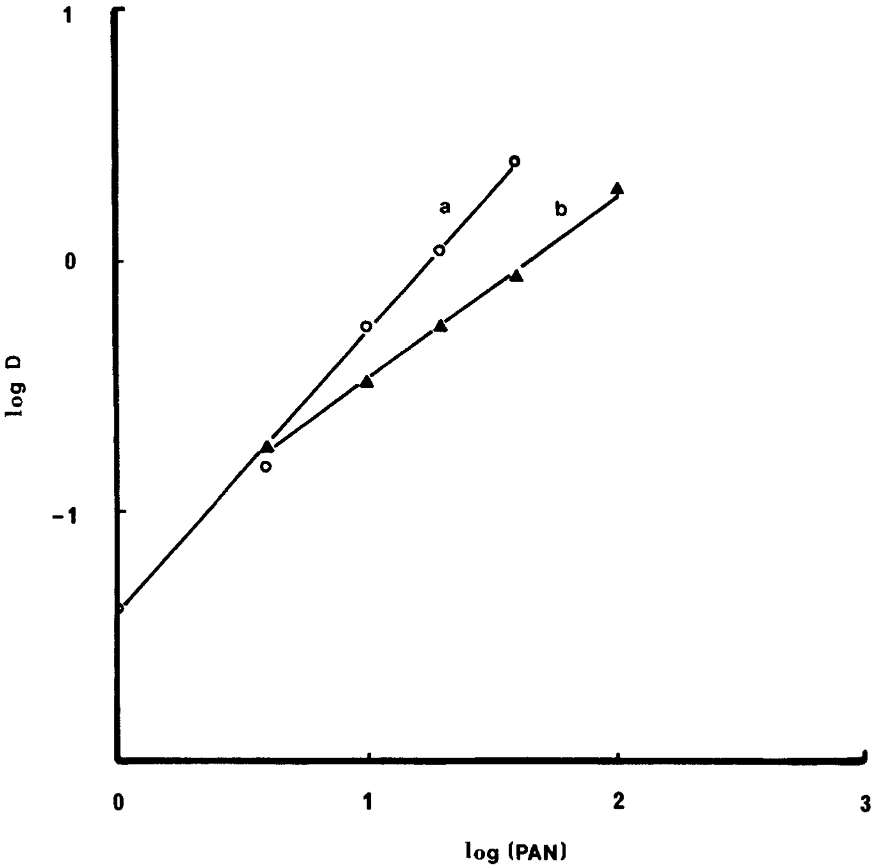


FIG. 1 Effect of PAN concentration on the extraction efficiency of nickel(II) (a, ○) and bismuth(III) (b, ▲) panate complexes in an aqueous: organic phase volume ratio of 1:1 with 5 μg nickel(II), 10 μg bismuth(III), 1 M $NaNO_3$, 3 M TBP, 0.5 M KSCN, pH 4, and a shaking time of 5 minutes.

ber of thiocyanate ions in the extracted species is determined by the slope method. The slopes of the plots (Fig. 4) indicate the presence of only one SCN ion in both cases. These results imply that a neutral Ni–PAN–SCN species is formed which is extractable in CCl_4 containing TBP. In the case of bismuth, however, a cationic Bi–PAN–SCN species is formed which undergoes association with an anion X^-, yielding a neutral extractable species. The X^- anion can be hydroxide or nitrate. Accordingly, the formulas of the extracted species of nickel and bismuth are probably [Ni(PAN)SCN]·4TBP and [Bi(PAN)SCN]X·TBP, respectively.

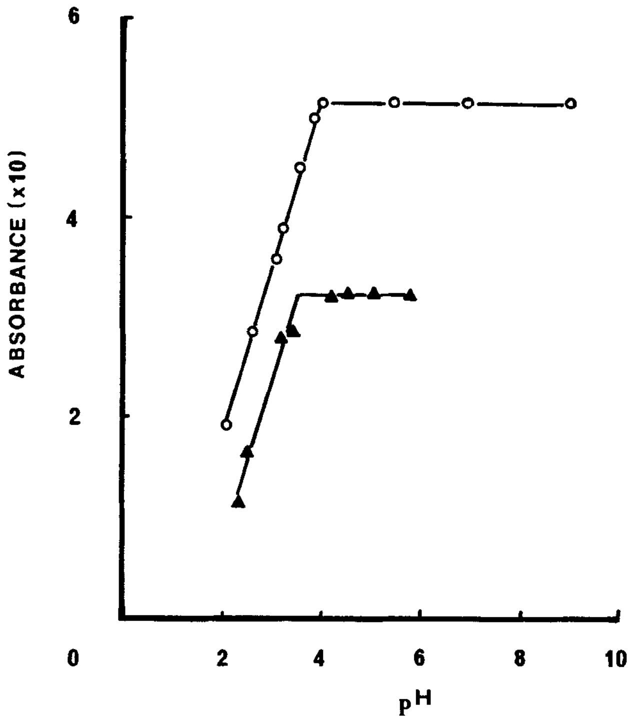


FIG. 2 Dependence of nickel(II) and bismuth(III) extraction efficiency (as panate complexes) on the medium's pH. Experimental settings and figure symbols as in Fig. 1. PAN concentration: 0.002% in 2.88 M TBP.

The absorption spectra of the extracted nickel- and bismuth-panate complexes show maxima at 560 and 565 nm, respectively. Beer's law is obeyed in the concentration ranges 0.1–1.0 and 0.4–4.0 $\mu g \cdot mL^{-1}$ for nickel and bismuth, respectively. The molar absorbances ϵ of the extracted nickel- and bismuth-panate complexes are 6.0×10^4 and 3.6×10^4 $L \cdot mol^{-1} \cdot cm^{-1}$, respectively. Sandell sensitivity indices S are 0.001 and 0.006 $\mu g \cdot cm^{-2}$ for nickel and bismuth, respectively. These results are considerably better than those reported in the literature for the spectrophotometric determination of nickel (15) ($\epsilon = 5.3 \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$; $S = 0.0011$ $\mu g \cdot cm^{-2}$) and bismuth (7) ($\epsilon = 1.88 \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$; $S = 0.011$ $\mu g \cdot cm^{-2}$) with PAN using other solvents. Thus, PAN in TBP solution can be employed for sensitive extractive spectrophotometric determination of nickel and bismuth in aqueous thiocyanate solutions. Worth noting is that the color of the nickel and bismuth extracts is maintained for 3 hours.

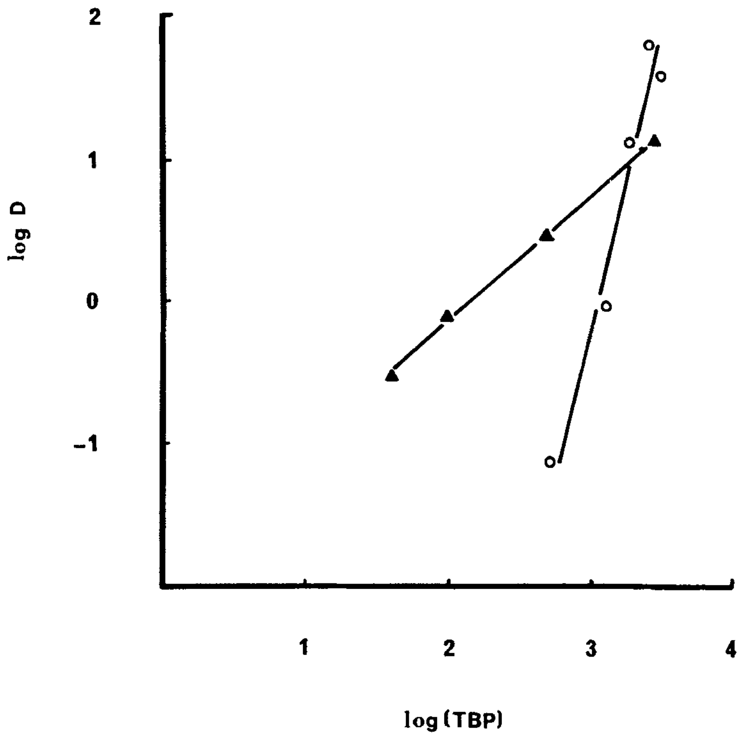


FIG. 3 Effect of TBP concentration on the distribution ratio of nickel– and bismuth–panate complexes. Experimental settings and figure symbols as in Fig. 2. The medium's pH is ~4.

At this stage it was decided to examine nickel and bismuth extraction and separation from aqueous thiocyanate media using a liquid–solid extraction system. In a previous work (16) open cell polyurethane foams proved to be successful for the impregnation of PAN solution in TBP. The most remarkable and advantageous quasispherical membrane structure of the foam material allows a rapid collection of nickel and bismuth from aqueous thiocyanate media onto PAN–foam columns.

Quantitative retention and recovery of nickel and bismuth were examined by a PAN–foam column. Thus, in separate experiments, when 10 μg nickel or bismuth in 0.2 M thiocyanate solution containing 1% $NaNO_3$ was introduced to the PAN–foam column, both complexes were retained as a narrow red band just on top of the column material. Each metal complex was recovered with 50 mL acetone at a flow rate of 5 mL·min^{-1}. After evaporation of acetone on a boiling water bath and upon acid digestion of the residue, nickel and bismuth were determined spectrophotomet-

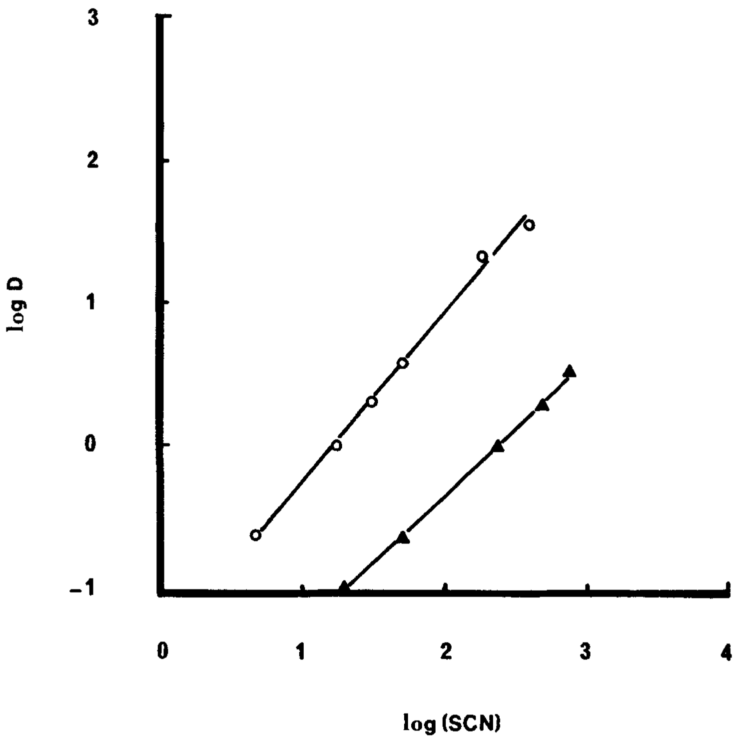


FIG. 4 Effect of thiocyanate concentration on the distribution ratio of nickel– and bismuth–panate complexes. Experimental settings and figure symbols as in Fig. 3. TBP concentration: 2.88 M.

rically (2) using dimethylglyoxime and dithiazone, respectively. Relative standard deviations for five extraction and recovery processes were found to be 1.2 and 1.6% for 10 μg nickel and bismuth, respectively. The relative errors were found to be 0.8 and 1.0% for the retention and recovery of nickel and bismuth, respectively.

The practical utility of PAN-loaded foam columns was tested by studying their ability for separating nickel or bismuth quantitatively from other metal ions, e.g., Fe^{3+}, Cd^{2+}, and Mn^{2+}.

Separate experiments for each element showed that Mn^{2+}, Cd^{2+}, and Fe^{3+} are quantitatively extracted from aqueous thiocyanate media by the PAN-loaded foam column. When a foam column (12 cm long and 15 mm i.d.) was used at a flow rate of 5 mL·min^{-1}, it was possible to separate a mixture of Ni^{2+} and Fe^{3+} by adding NaF for masking Fe^{3+} and preventing its extraction by the PAN–foam. Iron moved with the solvent front, while nickel was completely retained. Nickel was then recovered with acetone.

Separation of binary mixtures of Ni^{2+} or Bi^{3+} and Mn^{2+} or Cd^{2+} was achieved by eluting Cd^{2+} or Mn^{2+} with an acetate buffer (pH 4.5), followed by recovery of the nickel or bismuth complex with acetone.

Separation of a mixture of Mn^{2+}, Fe^{3+}, and Ni^{2+} was made in the light of the fact that in the presence of fluoride ions, Fe^{3+} moved first with the solvent front while both Mn^{2+} and Ni^{2+} are retained quantitatively on the foam column. Manganese is then eluted with acetate buffer (pH 4.5), and nickel is eventually recovered with acetone.

The proposed PAN–foam column was found to be useful for the preconcentration of small amounts of nickel or bismuth from dilute aqueous solutions. The passage of portions of a liter solution containing 10 μg of nickel or bismuth in 0.2 M thiocyanate, adjusted to pH 9 or 4, respectively, through a short column has effected 95–97% retention of nickel or bismuth by the column. The short column was 15 cm long, had 25 mm i.d., and was packed with 5 g PAN-loaded foam. The flow rate was 5–7 $mL\cdot min^{-1}$.

One of the attractive applications of reagent foams is their sensitive detection and semiquantitative determination of different inorganic species in aqueous media (10). A detailed study using PAN–foam for the selective detection and semiquantitative determination of nickel and bismuth in aqueous thiocyanate media has been undertaken.

A study of the effect of pH on the development of the red nickel and bismuth complexes with PAN–foam showed that pH 6 and 4 are most suitable for the detection of 1 μg of nickel and bismuth in 0.2 M thiocyanate solution, respectively. The red color was developed after shaking for 1–2 minutes, with a constant color intensity over the thiocyanate concentration range 0.1–0.5 M.

On shaking a foam cube with a 2-mL nickel or bismuth solution in a test tube, it was possible to detect 0.05 ppm nickel and 0.5 ppm bismuth within 1–2 minutes. In aqueous solutions containing lower concentrations of nickel (0.01 ppm) or bismuth (0.05 ppm), the PAN–foam test showed positive results when 25 mL of the sample solution was shaken in a stoppered flask.

PAN–foam was successfully employed for the detection of 1 μg of nickel in the presence of 10 mg chromium(VI), lanthanum(III), silver(I) acetate, oxalate, tartrate, ascorbate, phosphate, chlorate, sulfite, fluoride, bromide, or iodide. The PAN–foam test of bismuth (1 μg) also was possible in the presence of 10 mg of manganese(II), lead(II), lanthanum(III), silver(I), barium(II), thiosulfate, persulfate, phosphate, chlorate, ascorbate, bromide, or cyanide. Cadmium(II), zinc(II), manganese(II), iron(III), and bismuth(III) interfere in the test of nickel. On the other

TABLE 1
Detection of Nickel(II) with PAN–Foam in the Presence of Interfering Ions

Foreign ions	Compound added	Tolerance limit	Note
VO_3^-	NH_4VO_3	$1:1 \times 10^3$	Add few crystals of NaF
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	1:1	Add few crystals of thiourea
Cr^{3+}	$CrCl_3 \cdot 6H_2O$	$1:1 \times 10^3$	Add few crystals of sodium tartrate
Hg^{2+}	$Hg(NO_3)_2 \cdot H_2O$	$1:1 \times 10^3$	Add few crystals of $NaNO_2$
Ga^{3+}	$Ga(NO_3)_3$	$1:1 \times 10^4$	Add few crystals of NaF
Ba^{2+}	$BaCl_2 \cdot 2H_2O$	$1:1 \times 10^3$	Add 1 mL saturated solution of Na_2SO_4
Zr^{4+}	$Zr(NO_3)_4$	$1:1 \times 10^3$	Add few crystals of NaF

hand, mercury(II), barium(II), nickel(II), iron(III), chromium(VI), acetate, oxalate, tartrate, citrate, vanadate, thiosulfate, and iodide interfere in the test of bismuth. In the presence of some other ions, modifications of the aqueous solution are required for clear detection of nickel and bismuth (see Tables 1 and 2).

Semiquantitative determinations of nickel(II) and bismuth(III) are possible by comparison of the color intensity of the foam cube with standards prepared with 0.05, 0.10, 0.50, 1.00, and 5.00 ppm for nickel and 0.5, 1.0, 5.0, and 10.0 for bismuth under typical experimental conditions.

Lower concentrations of nickel (0.005 ppm) or bismuth (0.02 ppm) can be identified in flow experiments by percolating 100 mL of the nickel or bismuth solution through the reagent foam column at a flow rate of 5–7 $mL \cdot min^{-1}$. The length of the colored zone is proportional to the concentration of nickel or bismuth that can be estimated using standards covering concentrations of 5, 10, 20, 30, 40, and 50 ppb ($ng \cdot mL^{-1}$) for nickel and 20, 40, 60, 80, and 100 ppb for bismuth.

In conclusion, a PAN solution in CCl_4 containing TBP, in self-supported or immobilized modes, is advantageously used for sensitive detection,

TABLE 2
Detection of Bismuth(III) with PAN–Foam in the Presence of Interfering Ions

Foreign ions	Compound added	Tolerance limit	Note
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	$1:1 \times 10^4$	Add 1 mL of 1% KCN solution
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	$1:1 \times 10^4$	Add 1 mL of 1% KCN solution
Zn^{2+}	$Zn(NO_3)_2$	$1:1 \times 10^3$	Add 0.2 mL of 0.1 M HCl
Ga^{3+}	$Ga(NO_3)_3$	$1:1 \times 10^3$	Add 1 mL of 1% KCN solution
F^-	NaF	$1:5 \times 10^2$	Add few crystals of $CaCl_2$

quantitative separation, and spectrophotometric determination of nickel(II) and Bi(III) in aqueous thiocyanate media.

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