

NOTES

TABLE 2—IR, ^1H AND ^{19}F NMR SPECTRAL DATA OF COMPOUNDS 3

Sl. no	ν_{max} (KBr; cm^{-1})				^1H δ (DMSO- d_6 ; from TMS)			^{19}F δ	
	NH (br)	C_5N_3	C-Cl	CF_2 (asym.) (sym.)	C-NO $^+$ (asym.) (sym.)	NH (m)	ArH (m)		COOH OH OCH $_2$ OCH $_2$ CH $_2$ CH $_2$ C-CF $_3$
1.	3 360-3 110	820	795	1 125, 1 170 1 330	1 570 1 345	9 65-10.18	7 17-8.84	10 96(s)	-55.54
2.	3 380-3 100	800	770	1 125, 1 170 1 330	1 580 1 345	9 41-10.06	7 31-8.79	10 92(s)	-56 20
3.	3 380-3 100	805	775	1 125, 1 170 1 330	1 575 1 335	9.39-10.03	7.38-8.85	—	-55.48
4.	3 360-3 100	800	775	1 125, 1 170 1 330	1 570 1 335	9.61-10.05	7.38-8 81	9 61-10.05	-55.48
5.	3 360-3 120	815	795	1 130, 1 165 1 330	1 565 1 335	9.81-10.89	7.34-8 81	—	-55.54
6.	3 370-3 120	800	770	1 130, 1 170 1 330	1 575 1 345	9.85-10.12	7 03-8.78	3.88(s)	-55.18
7.	3 370-3 110	800	795	1 120, 1 165 1 330	1 570 1 340	9.95-10.89	6.59-8.14	4.12(q) 1.44(t)	-55.77
8.	3 360-3 100	800	775	1 125, 1 165 1 330	1 570 1 345	9 85-10.45	6.64-8 10	—	-55.57
9.	3 360-3 110	800	775	1 125, 1 165 1 330	1 575 1 340	9.15-10.05	6.62-8 20	2.68(s)	-56.57
10.	3 370-3 100	800	775	1 125, 1 170 1 330	1 575 1 340	9.78-10.85	7 30-8.84	—	-55.77

br = broad, s = singlet, m = multiplet, asym. = asymmetry, sym. = symmetry

dried and recrystallised from ethanol, (7.98 g, 93%), m.p. 259°.

2-Chloro-4-(2-chloro-5-trifluoromethylanilino)-6-(3-nitroanilino)-1,3,5-triazine (2): To 1 (3.43 g, 0.012 mol) dissolved in acetone (40 ml) was added a solution of 3-amino-4-chlorobenzotrifluoride (2.35 g, 0.012 mol) in acetone (10 ml) with continuous stirring followed by the addition of NaOH solution (0.48 g, 0.012 mol in 10 ml of water). It was stirred for 3 h at 30-35°. After cooling, the reaction mixture was poured into ice-cold water and acidified with HCl. The resulting solid was washed, dried and recrystallised from ethanol, (4.33 g, 81%), m.p. 230°.

2-(Arylanilino)-4-(2-chloro-5-trifluoromethylanilino)-6-(3-nitroanilino)-1,3,5-triazine (3): To 2 (0.003 mol) dissolved in 1,4-dioxane (6 ml), the solution of different aromatic amines (0.003 mol) in dioxane (6 ml) was added slowly followed by the addition of NaOH solution (0.003 mole in 5 ml of water). It was then heated for 3 h at 85-90°. After cooling, it was poured into ice-cold water. The resulting solid was washed, dried and recrystallised from ethanol (Tables 1 and 2).

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Determination of Bismuth at Parts per Million Levels in Rocks and Minerals by Flame Atomic Absorption Spectrometry

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FLAME atomic absorption methods for determination of bismuth at ppm levels in geological materials are subject to serious matrix interferences and their sensitivity is also not sufficient to permit direct measurements at such low levels^{1,2}. Donaldson³ proposed a Flame AAS method for determination of bismuth employing DDTC-chloroform extraction for removal of interferences, and proposed⁴ an iodide extraction method with improved performance. This method is also subject to interference from copper and lead, if present in large amounts. We have found that Flame AAS measurements directly from the organic phase provide much better sensitivity without any

increase in instrumental noise or interference. In this paper, we have described an iodide extraction procedure with methods for removal of copper and lead, where necessary, and Flame AAS measurements directly from the organic extract. The proposed method is suitable for determination of bismuth at ppm levels in a wide range of geological samples with reasonable precision and accuracy.

Experimental

Standard bismuth solution ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving metallic bismuth (99.9% purity) in dilute HNO_3 . Further dilutions were made before use using dilute HNO_3 (1N). TOPO-MIBK reagent (2%) was prepared by dissolving tri-n octylamine phosphine oxide in methyl isobutyl ketone. All chemicals used were of A.R. grade.

A Varian AA-6 atomic absorption instrument with Varian H.C. lamps was used for the atomic absorption measurements at 223.1 nm line using air-acetylene flame and standard operating conditions.

Sample decomposition and preparation of the main solution: Powdered sample (1 g) was mixed with HNO_3 (10 ml) and heated to dryness on a hot-plate. HF (15 ml) and HClO_4 (5 ml) were then added to the dry mass and again heated to dryness—the procedure was followed twice. Finally, the mass was dissolved in HCl (20 ml; 1:1, v/v) in case of silicate materials or in dilute HNO_3 (20 ml; 1:1 v/v) in case of sulphide ores. The solution was diluted to 100 ml.

Treatment of the main solution in case of copper sulphide ores: An aliquot of the main solution containing 5–50 μg of bismuth was diluted to about 100 ml, iron(III) solution (5 ml; $1000 \mu\text{g ml}^{-1}$) added and the mixture treated with dilute ammonia solution until distinctly ammoniacal. A 5 ml ammonia solution was then added in excess and the mixture boiled for 1 min. It was cooled to room temperature and filtered. The residue was washed several times with ammonia solution and dissolved in HCl (10 ml; 1:1, v/v). The solution was set aside for liquid-liquid extraction and FAA measurements for bismuth.

Treatment of the main solution in case of lead sulphide ores: An aliquot of the main solution containing 5–50 μg of bismuth was diluted with water to about 100 ml, heated to boiling and the hot solution treated with H_2SO_4 (5 ml, 1:5, v/v) with stirring. The mass was then cooled to room temperature and filtered. The residue was washed several times with hot water. The filtrate and washings were evaporated to a volume of about 50 ml and preserved for liquid-liquid extraction and FAA measurement for bismuth.

Liquid-liquid extraction and FAA measurements: The solutions obtained after separation of copper and lead in case of copper/lead sulphide ores or an

aliquot of the main solution (5–50 $\mu\text{g Bi}$) in case of silicate rocks/zinc ores was treated with HCl (5 ml) and volume of the solution adjusted to about 60 ml. Ascorbic acid (2 g) and KI (1 g) were then added to it and the mixture was shaken with TOPO-MIBK reagent for 1 min. The phases were allowed to separate and the aqueous phase was rejected. The organic phase was received in anhydrous sodium sulphate. The supernate was used for FAA measurements.

For calibration, standard solutions containing 0, 5, 10, 15 and 20 μg of bismuth were mixed with HCl (10 ml) and diluted to a volume of 60 ml, followed by addition ascorbic acid (2 g) and KI (1 g) and extracted with TOPO-MIBK (5 ml) as described above.

Results and Discussion

Liquid-liquid extraction of bismuth as iodide complex is adversely affected by the presence of large amounts of copper or lead. So, it has been necessary to remove copper and lead wherever these are present in concentrations exceeding 0.1% in the original sample. The proposed separation procedures permit efficient recovery of bismuth without any detectable loss. The efficiency of the iodide extraction process for quantitative extraction of bismuth is also well-established and very few elements like Hg, Sb, Cd and In are expected to be extracted along with Bi. These elements are normally present in very low amounts in rocks and minerals and hence no interference from them is generally noticeable.

TABLE 1—DETERMINATION OF BISMUTH IN ROCKS AND MINERALS

Sample*	Bi found** $\mu\text{g/g}$
Copper sulphide ore-1 (Cu-4.1%) ^a	22
Copper sulphide ore-2 (Cu-22.5%) ^a	730
Copper sulphide ore-3 (Cu-12.3%) ^b	320
Copper sulphide ore-4 (Cu-5.7%) ^c	68
Lead sulphide ore-1 (Pb-15.2%) ^e	18
Lead sulphide ore-2 (Pb-35.4%) ^b	45
Polymetallic sulphide ore-1 (Cu-2.2%, Pb-0.48% Zn-1.63%) ^d	1230
Granite, B-26 ^e	2.5
Granite, B-2287 ^e	3.5
Lead-Zinc ore, MP-1a ^f	310 (320 ^g)
Molybdenum-tungsten ore, MP-2 ^f	0.25% (0.245% ^h)

*Procured from: ^aIngaldhalu area, Chitradurga, Karnataka; ^bSinghbhum, Bihar; ^cSagipalli area, Orissa; ^dRangpo area, Sikkim; ^ePurulia, West Bengal; ^fCANMET.

**Recommended value from CANMET Report: ^g82-14E, 1982; ^h83-14E, 1983.

The proposed method has been applied to the determination of bismuth in a number of materials and the results are presented in Table 1. Two standard reference samples MP-1a and MP-2 (CANMET) have also been analysed for bismuth by this method and the results have been compared with the reported values. Precision studies by replicate analysis of one granite sample (B-26) also gave satisfactory results (RSD-6.5%). Recovery has also been checked by standard addition method.

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Extractive Spectrophotometric Determination of Trace Amounts of Zinc with Diphenylcarbazone in Presence of Pyridine

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DIPHENYLCARBAZONE has long been known as a reagent for the detection and determination of a number of metals¹⁻³. It forms chelate complexes with many heavy metals^{4,5}. Zinc(II) forms a purple coloured 1 : 2 complex⁶ with it, but the complex is not easily extractable. In the present investigation it is found that in presence of pyridine, zinc(II) forms with diphenylcarbazone a purple coloured complex which is completely extractable into methyl isobutyl ketone. This forms the basis of the present method which has proved to be very simple and sensitive.

Experimental

A Hilger-UVISPEK spectrophotometer with matched quartz cells of 1 cm optical path was used for absorbance measurements, pH values were determined with a Elico LI-10 pH-meter.

A stock solution of zinc was prepared from zinc metal (AnalaR) and was standardised by complexometric method⁶. The solutions of lower concentrations were prepared by appropriate dilution of the stock solution. A 0.3% solution of

diphenylcarbazone was prepared in absolute ethanol. A 5% pyridine solution in distilled water was used. Solutions of 0.2 M boric acid, 0.2 M potassium chloride and 0.2 M sodium hydroxide were prepared to constitute the required buffer. Standard solutions of diverse ions were prepared from their chloride, nitrate or sulphate or from sodium, potassium or ammonium salts.

Procedure : To an aliquot of the test solution containing 0.1 to 10 μg of zinc, 5% pyridine (2 ml) and buffer solution (2 ml) were added and the total volume was made upto 10 ml so that pH of the aqueous phase was around 10.0. To it, solutions of 0.3% diphenylcarbazone (1 ml) and MIBK (10 ml) were added and the resulting mixture was shaken for 5 min. The organic layer was separated and the absorbance of the extract was measured at 520 nm against the reagent blank. The zinc content was computed from the standard calibration curve.

Results and Discussion

The purple coloured zinc(II)–diphenylcarbazone–pyridine complex system extractable into MIBK, exhibits maximum absorbance at 520 nm when measured against the reagent blank and obeys Beer's law over the range 0.01–1 ppm of Zn^{2+} . The Sandell's sensitivity of the colour reaction is 0.00078 $\mu\text{g cm}^{-2}$ and molar absorptivity $8.37 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 520 nm. It was found that 0.3% diphenylcarbazone (1 ml) and 5% pyridine (2 ml) were adequate for complete extraction of zinc (0.1–10 μg) in the pH range 9.0–10.0 by a single extraction with 10 ml of MIBK. A 0.2–1% diphenylcarbazone and a 1–15% pyridine can be used without any adverse effect to absorbance value. The extracted species exhibited constant and maximum absorption when pH of the aqueous phase was maintained in the pH range 9.0–10.0. Various solvents such as 1,2-dichloroethane, chloroform, carbon tetrachloride, benzene, toluene, amyl alcohol and MIBK were tested for extraction of zinc complex, but MIBK was found to be the most effective one. With 10 ml of MIBK, the complex is recovered to the extent of 99.8% by a single extraction. The complex is stable for more than 24 h in MIBK. For complete extraction of the complex, 5 min shaking period was adequate. The absorbance of the complex is independent of temperature in the range 12–35°. Job's method of continuous variation⁷ and mole-ratio method⁸ indicated that a 1 : 2 complex between zinc and diphenylcarbazone is formed. The complex seems to have been stabilised by mixed ligation with pyridine.

Effect of diverse ions : The effect of different foreign ions in the determination of zinc (5 μg) was studied. The tolerance limit was set at the amount required to cause less than 3% error in the recovery of zinc. Estimation of zinc in presence of Cu^{2+} was done using thiourea as