

Use of Malathion for High Performance Liquid Chromatographic Determinations of Bismuth(III), Copper (II) and Palladium(II), Based on Complexation with Dimethyl Dithiophosphate

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Summary: Malathion in alkaline solution is hydrolysed to dimethyldithiophosphate (DDTP), which is used as a complexing reagent for the HPLC separation and quantitative determination of bismuth(III), copper (II) and palladium (II) in a mixture. The complexes extracted in chloroform are eluted from normal phase HPLC column (250 x 4 mm id) Licrosorb Si, 100, 5 μ , with chloroform:acetonitrile:1,2-dichloroethane (25:70:5 v/v/v) with a flow rate 0.8 ml/min. The detection was at 295 nm. Linear calibration for each of bismuth(III), copper(II) and palladium(II) were obtained with 12.5-62.5 μ g/ml of chloroform and detection limits were 0.1-0.2 ng/injection. The method was applied for the determination of copper in copper wires and palladium in palladium-barium sulphate.

Introduction

A number analytical methods are available for the determination of copper, bismuth and palladium including spectrophotometric, atomic absorption spectrometric and electro-analytical methods. High performance liquid chromatographic (HPLC) methods are interesting because of the capability for simultaneous determinations at μ g levels when an appropriate complexing reagent is employed. For HPLC determination of bismuth, copper and palladium a number of complexing reagents have been suggested mainly acetylacetone [1], dithiocarbamate [2-4], nitrosonaphthol derivatives [5], tetradentate Schiff bases [6,7], E.D.T.A. [8]

thiosemicarbazone [9] and different azo derivatives [10-13]. The present work examines the use of inexpensive organophosphorous pesticide malathion for the HPLC determination of bismuth, copper and palladium. The method is based on alkaline hydrolysis of malathion to dimethyl dithiophosphate (DDTP) and complexation of bismuth, copper and palladium with DDTP. The complexes are extracted in chloroform and chromatography is carried out from a normal phase Si, 100, HPLC column.

Organophorous pesticide malathion in formulations have indirectly been determined by

spectrophotometry [14,15], atomic adsorption [16-19] and HPLC [20-22], based on alkaline hydrolysis of malathion to DDTP, followed by complexation of DDTP with copper(II), bismuth(III) or palladium(II). HPLC has been carried out from normal or reverse phase columns coupled with UV detection.

Results and Discussion

Bismuth(III), copper(II) and palladium(II) form coloured complexes when excess of DDTP is added. The complexes are easily extractable in chloroform. The colour of bismuth(III) and palladium(II) is stable for longer time (24 hr) [15,16] but the colour of copper(II) in visible region is stable for short time [12,21]. However the absorbance is sufficiently stable in UV region (3 hr) to enable to record the chromatograms [21]. The bismuth(III), copper (II) and palladium(II) complexes eluted from normal phase HPLC column with chloroform as sharp and symmetrical peaks, but with little separation between bismuth, copper and palladium. Some separation between the metal DDTP complexes was obtained with binary mixtures of chloroform and 1,2-dichloroethane. However optimal separation was obtained using ternary mixture of chloroform:acetonitrile: 1,2-dichloroethane (25:70:5 v/v/v) with a flow rate of 0.8 ml/min and detection at 295 nm.

Response of UV monitor for simultaneous calibration was checked with different concentrations of bismuth, copper and palladium in mixtures using DDTP and malathion as complexing reagent. Same quantitative response was obtained following analytical procedure A and B (Fig. 1) and linear calibration curves were obtained by measuring average peak height ($n=3$) with five standards solution in the range 0-125 μg in an aliquot with coefficient of correlation (r) of 0.991, 0.9990 and 0.9995 for bismuth(III), copper(II) and palladium(II) respectively. The detection limit measured at least three times the background noise were 0.2, 0.2, 0.1 μg in 2 ml of extract in chloroform corresponding to 0.2 μg , 0.2 μg , 0.1 ng/injection (2 μl) for bismuth, copper and palladium respectively. Test mixtures of bismuth, copper and palladium were analysed and relative % error was found within $\pm 0-6\%$. The copper wires for copper contents and palladium barium sulphate for palladium contents were

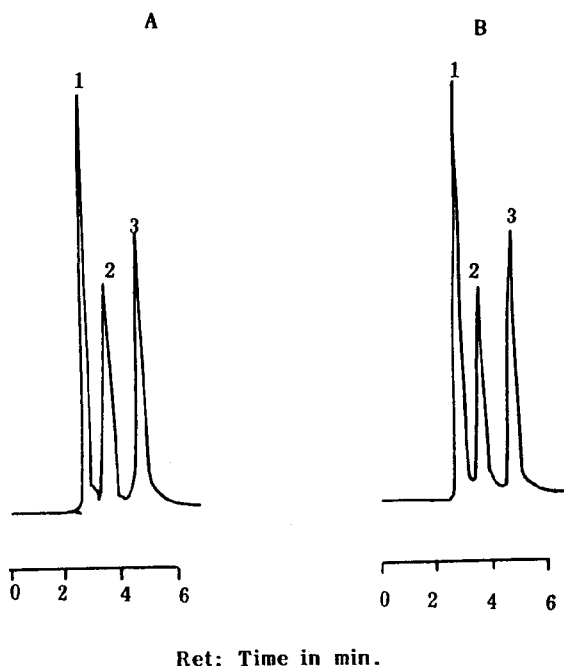


Fig. 1: HPLC separation of 1) palladium 2) copper (II) and (3) bismuth (III) A) using DDTP (B) Malathion. Concentration 50 μg each in an aliquot. Column Licrosorb Si, 100, 5 μ (250 x 4 mm id). Elution chloroform: acetonitriles: 1,2-dichloroethane (25:70:5 v/v/v) with flow rate of 0.8 ml/min. and detection at 295 nm.

analysed using HPLC method. The copper in copper wire was found 82% with coefficient of variation (C.V) 3.62% and palladium in palladium-barium sulphate was found 4.68% with C.V. 3.15%. The copper in copper wires was also analysed using atomic absorption and was found 78% with C.V. 1.2%.

Experimental

Dimethyldithiophosphoric acid (DDTP) was prepared as reported [23] by reacting methanol with phosphorus pentasulphide at room temperature. Bismuth(III), copper(II) and palladium(II) solution (1 mg/ml) were prepared from G.R. grade (E. Merck) bismuth(III) oxide, copper(II) sulphate and palladium(II) chloride. All the solvents and chemicals G.R. grade (Merck) were used without further purification.

A Hitachi 655A liquid chromatograph with variable wavelength UV monitor, Rheodyne 7125 injector and Hitachi D2500 chromatogram integration was used. A normal phase column (250 x 4 mm id) Licrosorb Si, 100 μ m was used through out the study. Varian Spectr AA-20 atomic absorption spectrometer with air-acetylene flame atomizer with standard burner head was used. The analysis was carried out in triplicate with delay time 3 sec. and integration time 3 sec.

A. Solvent extraction procedure

To a well stoppered test tube was transferred (1-5 ml) containing copper(II), bismuth(III) and palladium (25-125 μ g each) followed by DDTP (1 ml, 1% in ethanol) and hydrochloric acid (7M, 2 ml). Chloroform (2.0 ml) was then added and contents were mixed well. The layers were allowed to separate and a portion of the organic layer was transferred to sample vial and solution (2.0 μ l) was injected on normal phase HPLC column Licrosorb Si, 100 μ m (250x4 mm id). The complexes were eluted isocratically with chloroform:acetonitrile: 1,2-dichloroethane (25:70:5 v/v/v) using flow rate of 0.8 ml/min. The detection was at 295 nm.

B. Solvent extraction procedure using malathion

Malathion emulsifiable insecticide dust (malathion 57% F.G) (Malacheme Co. Iran) (2 g) dissolved in ethanol was added (4 ml, 6N) sodium hydroxide. The contents were shaken for 5-7 min and volume was made to 100 ml. The solution (1 ml) was added to the well stoppered test tube containing bismuth(III) copper(II) and palladium(II) (25-125 μ g) each in 1-5 ml solution. The contents were added hydrochloric acid (2 ml, 7M) and extraction procedure was followed as A.

Analysis of copper in copper wires

Copper wire (1.0 g) was added hydrochloric acid (37%) (10 ml) and nitric acid (65%) (5 ml) and contents were heated to near dryness. Hydrochloric acid (37%) (5 ml) was added and was again heated to near dryness. The residue was dissolved in water and volume was adjusted to 100.0 ml. Solution (1 ml) was further diluted to 100.0 ml and solution 0.5 ml and 1.0 ml was taken and solvent extraction procedure A or B was used. The amount of copper in

copper wires was evaluated from the calibration curve prepared from the known amounts of copper(II). Copper in copper wires was also analysed using flame atomic absorption spectrometer at 324.8 nm.

Analysis of palladium in palladium-barium sulphate

Palladium 5% on barium sulphate (Sigma Chemical Company) (0.5 g) was added hydrochloric acid (37%) (10 ml) and was gently heated to 2-3 ml. Hydrochloric acid (3.0 ml) was again added and heated to about 2.0 ml. The solution was dissolved in water and solution was filtered and volume was adjusted to 100 ml. Solution (1.0 ml) was further diluted to 25.0 ml. Solution (2.0 ml) and (4.0 ml) was taken and extraction procedure A or B was used. The amount of palladium was calculated from calibration curve for palladium.

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