

Revers Phase Liquid Chromatographic Separation and Determination of Bismuth(III), Copper(II) and Palladium(II) using Dimethyl Dithiophosphoric Acid as Complexing Reagent

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Summary: Bismuth(III), Copper(II) and Palladium(II) complexes of dimethyl dithiophosphoric acid (DDTP) from acidic media are extracted in chloroform and separated on YMC ODS 5 μ m column (150 x 4.6 mm id), when eluted isocratically with a mixture of acetonitrile: methanol: water (70:20:10 v/v/v) with a flow rate 0.6 ml/min and detection at 295 nm. Linear calibration curve were obtained with 25-125 μ g aliquot of each of metal with detection limits of 0.4-0.8 ng/injection. The method is applied for the determination of copper in copper wires.

Introduction

A number of complexing reagents are reported for bismuth(III), copper(II) and Palladium (II) determinations using liquid chromatography (LC) connected with spectrophotometric detection, present in mixtures with different elements. Common among these are acetylacetone [1] dithiocarbamates [2-6] nitrosonaphthol [7], tetradentate Schiff bases [8-13], quinolin-8-ol, [14,15], thiosemicarbazones [16-18], E.D.T.A. [19] and different azo derivatives [20-28].

Dimethyl dithiophosphoric acid (DDTP) is a component of organophorous pesticides and has been determined by spectrophotometry [29,30], atomic absorption spectrometry [31-34] or liquid chromatography [35-37]. The present work examine DDTP as a complexing reagent for reverse phase LC determination of bismuth(III), copper(II) and Palladium(II).

Results and Discussion

DDTP reacts with bismuth(III), copper(II) and palladium(II) in acidic solution to form coloured complexes which are extractable in organic solvents including chloroform and carbon tetrachloride. Bismuth(III) and Palladium(II) complexes are reported to be highly stable [30-37], but absorbance of copper(II)-complex in visible region is stable for short time, but the absorbance in the UV is sufficiently stable (3 hr) to carry out HPLC studies [36].

Bismuth(III), Copper(II) and Palladium(II) complexes of DDTP easily eluted from reverse

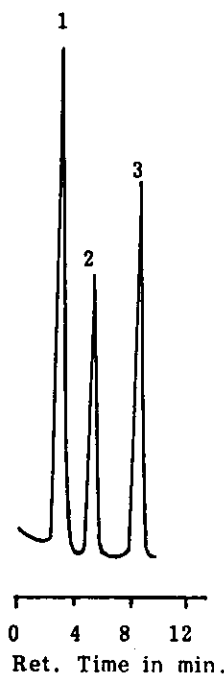


Fig. 1: HPLC Separation of (1) palladium(III) (2) copper(II) and (3) bismuth(III) column YMC, ODS, 5 μ m (150 x 4.6 mm id). Elution with acetonitrile; methanol: water(70:20: 10 v/v/v) with a flow of 0.6 ml/min with detection at 295 nm.

phase HPLC column YMC ODS, 5 μ , when eluted with methanol water or acetonitrile water, but complete and base line separation was obtained when eluted with acetonitrile:methanol: water (70:20:10 v/v/v) with a flow rate of 0.6 ml/min.

The detection was at 295 nm. The retention times for palladium, copper and bismuth complexes were 3.0, 5.40 and 8.60 min respectively (Fig. 1).

Linear calibration curves for simultaneous determination of bismuth(III), copper(II) and Palladium(II) were plotted by measuring average peak height ($n=3$) versus amount of metal ions in solution and were found linear in the range of 12.5-62.5 $\mu\text{g/ml}$, with coefficient of correlation (r) 0.999, 0.993 and 0.997 for bismuth, copper and palladium respectively (Fig. 2). The detection limits measured as three times the back ground noise were found 0.4 $\mu\text{g/ml}$, 0.4 $\mu\text{g/ml}$ and 0.2 $\mu\text{g/ml}$ corresponding to 0.8ng, 0.8ng and 0.4ng/injection (2 μl). Test mixtures of bismuth, copper and palladium were analyzed and amounts of metal ions were evaluated from the calibration curve and % relative errors were found within 0-4%. Finally a copper wire sample was analysed for the determination of copper contents after acid digestion and amount of copper found was 87.5%.

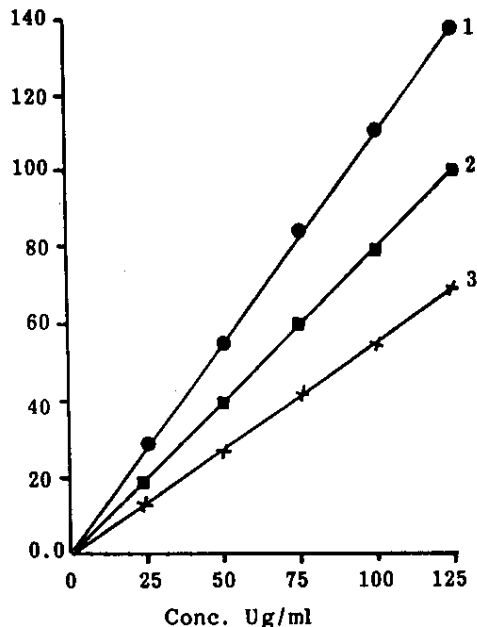


Fig. 2: Calibration curves of (1) palladium (II) (2) bismuth(III) (3) copper(II).

Experimental

Dimethyldithiophosphoric acid (DDTP) was prepared as reported [38] by the reaction of phosphorous pentasulphide with methanol.

Analytical procedure

To a well stoppered test tube (Quickfit) was transferred (1-5 ml) containing 25-125 μg each of bismuth(III), Copper(II) and Palladium(II) and DDTP was added (1 ml, 1% in ethanol), followed by hydrochloric acid (2 ml, 7M) and chloroform (2 ml). The contents were mixed well and layers were allowed to separate. Exactly organic layer (1 ml) was transferred to sample vial and solvent was evaporated and the residue dissolved in methanol (1 ml). Solution (2 μl) was injected on YMC ODS, 5 μ column and complexes eluted with acetonitrile: methanol:water (70:20:10 v/v/v) with a flow rate of 0.6 ml/min. The detection was made at 295 nm.

Analysis of copper in copper wires

Copper wire (1.0g) was added to 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 again heated to near dryness. The residue was dissolved in water and volume was diluted to 100 ml. Solution (1 ml) was further diluted to 100 ml and solutions 0.5 ml and 1 ml were taken and analytical procedure was followed. The amount in solution was evaluated from standard calibration curve.

A Hitachi model 655A liquid chromatograph connected with a variable wavelength UV monitor, Rheodyne 7125 injector and Hitachi D-2500 chromato-integrator were used.

Column YMC ODS, 5 μ (150x4.6 mm) (YMC, Japan) was used throughout the study.

Phosphorous pentasulphide (Fluka) and G.R. grade methanol, acetonitrile, hydrochloric acid (37%) and nitric acid (65%) (E.Merck) were used. Freshly prepared double distilled water was used for HPLC studies.

References

1. S. Ichinoki and M. Yamazaki, *Anal. Sci.*, **5**, 465 (1989).
2. S. Dilli, P.R. Hadded and A.K. Htoon, *J. Chromatogr.*, **500**, 313 (1990).
3. S. Comber, *Analyst*, **118**, 505 (1993).

4. R.V. Gonzalez, J.M. Castro Romero, J.M. Fernandez Solis, J. Perez Iglesias and H.M. Seco Lago, *Anal. Lett.*, **27**, 1399 (1994).
5. P.A. Steenkamp and P.P. Coetzee, *Fresenius, J. Anal. Chem.*, **346**, 1017 (1993).
6. H. Irth, G.J. De Jong, U.A.T. Brinkman, R.W. Frei, *J. Chromatogr.*, **482**, 317 (1989).
7. H. Siren, *Chromatographia*, **29**, 144 (1990).
8. M.Y. Khuhawar and G.Q. Khaskheli, *J. Chem.Soc.Pak.*, **13**, 10 (1991).
9. G. Chen, K. Zhu, S. Yuan, *Fenxi Huaxue*, **20**, 553 (1992).
10. M.Y. Khuhawar and R.B. Bozdar, *J. Chem. Soc. Pak.*, **13**, 197 (1991).
11. M.Y. Khuhawar and A.I. Soomro, *Anal. Chem. Acta.*, **268**, 49 (1992).
12. M.Y. Khuhawar and A.I. Soomro, *J. Liq Chromatogr.*, **15**, 647 (1992).
13. M.Y. Khuhawar and A.I. Soomoro, *J. Chromatogr.*, **639**, 371 (1993).
14. Y. Nagaosa, A.M. Bond, *J. High Resolut Chromatogr.*, **15**, 622 (1992).
15. E. Ryan, M. Meaney, *Analyst*, **117**, 1435 (1992).
16. M.Y. Khuhawar, Z.P. Memon, S.N. Langwani, *Chromatographia*, **41**, 236 (1995).
17. N. Vehara, K. Morimoto, Y. Shijo, *Analyst*, **117**, 977 (1992).
18. S. Hoshi, S. Kato, M. Nara, M. Matsubara, *Bunseki Kagaku*, **40**, 429 (1991).
19. G. Sacchero, O. Abollino, V. Porta, C. Sarzanini, E. Mentasti, *Chromatographia*, **31**, 539 (1991).
20. E.M. Basova, T. A. Bol Shoua, O.A. Shpigun, *Zh. Anal. Khim.*, **46**, 2362 (1992).
21. A.R. Timerbaev, O.M. Petrokhin, V.I. Orlov, A.A. Aratskova, *J. Lig Chromatogr.*, **15**, 1443 (1992).
22. J.R. Chen, S.M. Wu, *Fenxi Huaxue*, **22**, 974 (1994).
23. Y. Shijo and T. Shimizu, *Analyst*, **113**, 1201 (1988).
24. N. Uehara, Y. Annoh, T. Shimizu, Y. Shijo, *Anal. Sci.*, **5**, 111 (1989).
25. E.N. Shapovalova, I.V. Mishenina, E.M. Basova, T.A. Bol'shova, O.A. Shpigun, *Zh. Anal. Kim.*, **46**, 1503 (1991).
26. Q.P. Liu, Y.C. Wang, J.C. Liu, J.K. Cheng, *Fenxi Huaxue*, **20**, 1088 (1992).
27. Q.P. Liu, H.S. Zhang, J.K. Chang, *Fresenius J. Anal. Chem.*, **344**, 356 (1992).
28. H. Wang, Y.X. Miao, W.Y. Mou, S.H. Zhang, J.K. Chen, *Microchim. Acta*, **117**, 65 (1994).
29. K. Viswes wriah and M. Jayaram, *Agrl. Biol. Chem.*, **38**, 2031 (1974).
30. E.R. Clerk and I.A. Qazi, *Analyst*, **104**, 1129 (1979).
31. J. Hernandez Mendez, O. Jimenez de Blas, V. Rodri Guez Martin, E. Sanchez Lopez, *Anal. Lett.*, **18A**, 2069 (1985).
32. J. Hernandez Mendez, O. Jimenez de Blas and V. Rodriguez Martin, *Microchim. J.*, **37**, 275 (1988).
33. O. Jimenz de Blas, J.L. Pereda de Paz and J. Hernandez de Blas, *Analyst*, **114**, 1675 (1989).
34. O. Jimenez de Blas, J.L. Pereda de Paz and J. Hernandez Mendez, *Talanta*, **38**, 857 (1991).
35. M.Y. Khuhawar, A.H. Channar and S.N. Lanjwani, *Chromatographia*, **42**, 680 (1996).
36. M.Y. Khuhawar, A.H. Channar and S.N. Lanjwani, *J. Chromatogr A*, **758**, 159 (1997).
37. M.Y. Khuhawar, A.H. Channar and S.N. Lanjwani, *J. Chem. Soc.Pak.*, **18**, 306 (1996).
38. M.I. Kabachik and T.A. Mastryukova, *Invest. Akad. Nauk. SSSR, Didel Kim Nauk*, **121** (1953); *C.A.* **40**. 3244e (1954)