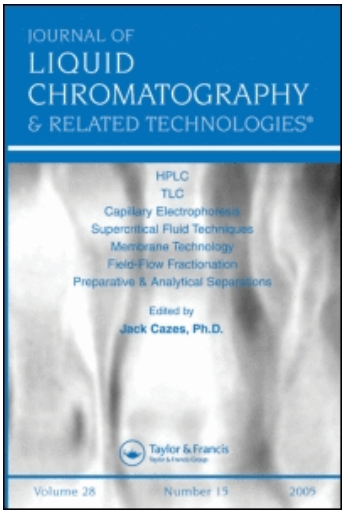

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Interference by Disodium Edetate with the Reaction of Phenylmercury Ions with Dithiocarbamate Derivatising Agents

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To cite this Article Parkin, J. E.(1992) 'Interference by Disodium Edetate with the Reaction of Phenylmercury Ions with Dithiocarbamate Derivatising Agents', Journal of Liquid Chromatography & Related Technologies, 15: 3, 441 — 449
To link to this Article: DOI: 10.1080/10826079208017183
URL: http://dx.doi.org/10.1080/10826079208017183

JOURNAL OF LIQUID CHROMATOGRAPHY, 15(3), 441-449 (1992)

INTERFERENCE BY DISODIUM EDETATE WITH THE REACTION OF PHENYLMERCURY IONS WITH DITHIOCARBAMATE DERIVATISING AGENTS

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ABSTRACT

The reaction of phenylmercuric nitrate with diethylamine-dithiocarbamate in the presence of disodium edetate has been investigated. Under these conditions the derivatisation reaction does not proceed cleanly but a portion of the phenylmercuric ion is converted to diphenylmercury with an equimolar amount of derivatised mercuric ion being produced. This reaction is independent of the disodium edetate concentration beyond a 1:1 mole ratio of phenylmercuric ion to edetate ion.

INTRODUCTION

Increasing interest is being taken in the analysis of organo-mercury compounds by high performance liquid chromatography (HPLC).[1-12] In these studies chromatography was achieved in the reverse-phase mode as an appropriate thiol derivative[2-6,8,10] or a dithiocarbamate[7,9,11] or dithizonate

complex[12] and detection was by electrochemical,[2,3,10] atomic absorption spectroscopy[4,6,8] or U.V. in the case of the dithiocarbameates.[7,9,11] This paper demonstrates that when derivatisation is performed using diethylaminedithiocarbamate (DEADTC) in the presence of disodium ethylenediaminetetraacetate (disodium edetate)(EDTA) that an unusual side-reaction occurs in which the PM ion is converted to mercuric ion and diphenylmercury (DPM).

MATERIALS

PM nitrate (BDH, UK), DPM (Fluka, FRG) were used in this study. All other chemicals were analytical grade. The diethylammonium salt of (DEADTC)[9,11] was prepared as reported previously and the reagent prepared by dissolving the salt (60 mg) in acetonitrile (100 mL). Standards for Hg^{2+} were prepared by the use of mercuric chloride.

METHODS

Chromatographic equipment and conditions

The liquid chomatograph consisted of a Model 501 pump (Waters Assoc., Milford, MA, USA), Rheodyne Model 7125 20 μL loop injector (Cotati, CA, USA), Model 484 variable-wavelength absorbance detector (Waters Assoc.) and Model 3396A integrating recorder (Hewlett-Packard, PA, USA) together with a column of octadecyl silica (Waters Assoc.) 30 cm x 3.9 mm i.d. 10 μm particle size. The monitoring wavelength was 258 nm. The solvent used was 75% acetonitrile containing 1 x 10^{-4} M EDTA at a flow-rate of 1.8 mL min^{-1}.

Spectrophotometric equipment

UV spectra were obtained using an HP 8450 UV-VIS spectrophotometer (Hewlett-Packard).

Preparation of samples for analysis

Unless otherwise specified 1 mL of solution to be analysed was transferred to a glass vial followed by 1 mL of DEADTC reagent. The solutions were then mixed thoroughly and allowed to stand for approximately 2 min. prior to analysis.

Preparation of standard curves

Solutions of PM nitrate and mercuric chloride over the concentration range 0-1.5 x 10^{-4}M were prepared and submitted to analysis as outlined above.

Effect of mole-fraction of EDTA on the derivatisation of PM nitrate

Solutions of PM nitrate (1 x 10^{-4}M) containing zero and a range of concentrations of EDTA from 0.4 x 10^{-5}M to 1.5 x 10^{-3}M were prepared and submitted to analysis as outlined above.

Effect of time following mixing on the extent of derivatisation in the presence and absence of EDTA

Solutions of PM nitrate and mercuric chloride (1 x 10^{-4}M) with and without EDTA (2 x 10^{-4}M) were prepared. 10 mL of these solutions were transferred to 25 mL tubes with screw-caps and PTFE wads. 10 mL of derivatising reagent was added and the resulting solution analysed at regular time intervals for 1 h.

Effect of time following mixing on the extent of derivatisation when EDTA is added last

To a solution of PM nitrate (2 x 10^{-4}) (5 mL) in a 25 mL tube with screw-cap and PTFE wad was added derivatising agent (10 mL) and 1 min. later EDTA (4 x 10^{-4}) (5 mL). The solutions were then analysed at regular time intervals for 1 h.

Identification and quantitation of DPM

A solution of PM nitrate (1 x 10^{-4}M) containing EDTA (2 x 10^{-4}M) was submitted to analysis for DPM by a previously reported method.[13] The

identity was confirmed by extracting the derivatised solution (10 mL) with ether (5 mL) and transfer of the ether layer to a conical tube and evaporation in a stream of nitrogen. The residue was then dissolved in acetonitrile (0.5 mL) and the solution submitted to chromatography[4] and a UV spectrum was obtained using a diode-assay spectrophotometer in series with the detector.

RESULTS AND DISCUSSION

The addition of DEADTC reagent in acetonitrile to a solution of PM nitrate to be analysed affords a stable PM.DEADTC complex which is readily chromatographed. In studies of the stability of PM nitrate in the presence of EDTA an immediate loss of PM.DEADTC occurred with the formation of the Hg $(DEADTC)_2$ complex (Fig. 1 A-C).

The chromatographic conditions afford resolution of the complexes derived from the PM and Hg^{2+} ions and the method was validated for both PM and Hg^{2+} complexes over the concentration range of 0 - 1.5 x 10^{-4} M. For PM nitrate r = 0.9996, (n = 6) with a CV of ± 1.4% (n = 6) at a concentration of 4 x 10^{-5} M and for Hg^{2+} salts: r = 0.9999 (n = 6) with a CV of ± 0.6% (n = 6) at a concentration of 4 x 10^{-5} M.

The extent of this side-reaction to the derivatisation process reaches a maximum at approximately a 1:1 mole-ratio of PM nitrate to EDTA and remains unchanged at ratios above this value (Fig. 2). Subsequent studies have therefore been conducted at a mole-ratio of 1:2 of PM nitrate to EDTA. Studies of the reaction against time following mixing of the reagent shows that the reaction occurs during derivatisation and the product mix subsequently remains unchanged (Fig. 3D). Also, the $Hg(DEADTC)_2$ formed accounts for only half of the losses of PM.DEADTC (Fig. 3D). Further, PM nitrate and Hg^{2+} in the absence of EDTA afford the expected stable complexes in quantitative amounts (Fig. 3 A, B). Addition of EDTA after the initial formation of the complex with PM nitrate demonstrates that the PM.DEADTC complex, once formed, is stable and is not influenced by the presence of EDTA (Fig. 3 C). This is important as in these studies EDTA has been added in low concentration to the chromatographic solvent to minimise interference from trace amounts of other ions.[6]

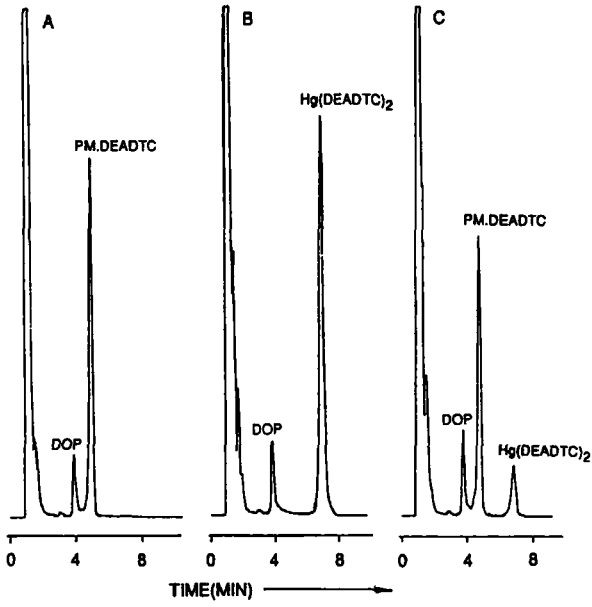

FIGURE 1

Representative chromatograms. A: PM nitrate (1×10^{-4} M); B: $HgCl_2$ (1×10^{-4} M); C: PM nitrate (1×10^{-4} M) containing EDTA (2×10^{-4} M) (0.064 a.u.f.s., monitoring wavelength 258 nm). Peaks: 4.8 min, PM-DEADTC complex; 6.9 min, $Hg(DEADTC)_2$ complex; 3.7 min, disulphide oxidation product arising from slow atmospheric oxidation of the reagent (DOP); excess DEADTC reagent elutes at the void volume.

Further chromatographic investigations demonstrated that the mercury not accounted for occurs as DPM which has been quantitated by a chromatographic procedure reported in a previous study[13] and corresponds to a mole-fraction of 0.119 (n = 3). This fully accounts for the total amount of mercury available in the system [Mole fraction: PM.DEADTC = 0.721; $Hg(DEADTC)_2$ = 0.131; DPM = 0.119; TOTAL = 0.971]. The identity of the DPM was confirmed by comparison of a UV spectrum obtained from the DPM with that of an authentic sample of DPM obtained in a similar manner using a diode-array spectrophotometer in series with the HPLC system.

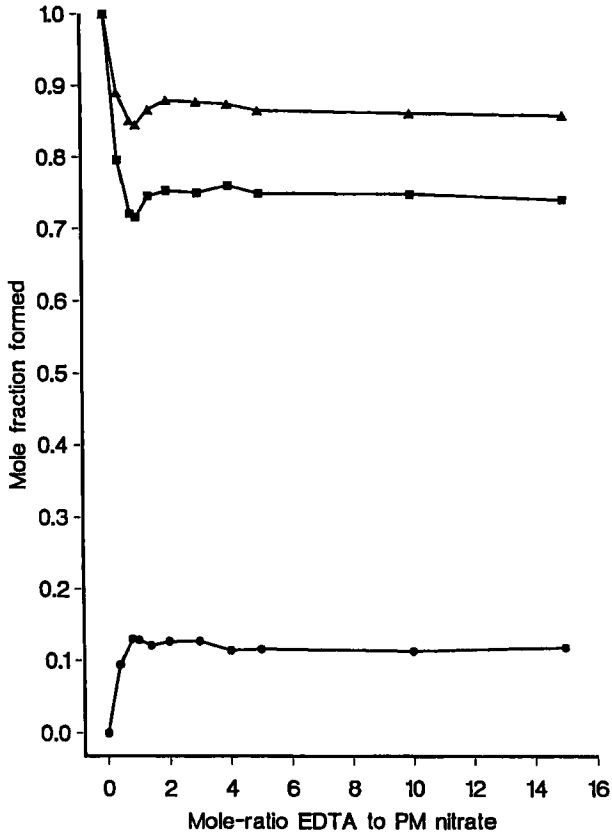

FIGURE 2

The influence of the mole-ratio of EDTA to PM nitrate (1×10^{-4} M) on the extent of formation of PM.DEADTC and Hg $(DEADTC)_2$. ■: PM.DEADTC; ●: Hg $(DEADTC)_2$; ▲: total PM.DEADTC + Hg $(DEADTC)_2$

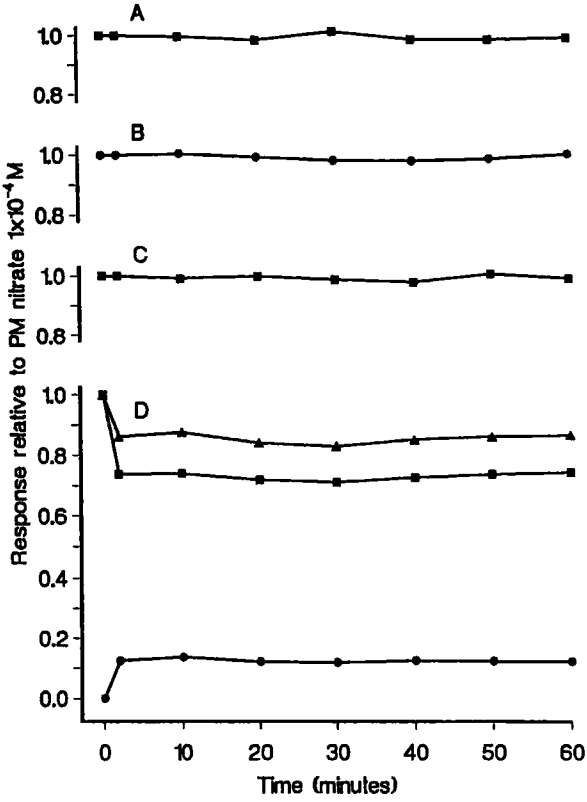

FIGURE 3

The effect of time following mixing on the response relative to PM nitrate (1 x 10^{-4} M). A: PM nitrate (1 x 10^{-4} M); B: $HgCl_2$ (1 x 10^{-4} M); C: PM nitrate (1 x 10^{-4} M) in which the EDTA (2 x 10^{-4} M) is added after the DEADTC reagent. D: PM nitrate (1 x 10^{-4} M) containing EDTA (2 x 10^{-4} M). ■: PM.DEADTC; ●: Hg $(DEADTC)_2$; ▲ total PM.DEADTC + Hg $(DEADTC)_2$

Possible interpretations of these results are either that the reaction proceeds between PM nitrate and EDTA prior to the addition of the complexing agent and that the analytical results reflects an established range of products in the solution to be analysed or that the reaction proceeds concurrently with the complexation reaction as a side-reaction. PM nitrate has therefore been analysed by a previously reported method involving prior ether-extraction of the PM ion as PM chloride followed by derivatisation isolating the derivatisation process from the lipid-insoluble EDTA.[14] Under these conditions no loss of PM nitrate occurred in the presence of EDTA (99.0% of theoretical, n = 3). Therefore, the reaction to form DPM and Hg $(DEADTC)_2$ occurs as a side-reaction to the formation of PM.DEADTC.

There is no previous report of this reaction occurring. However, the reaction of aryl-mercury salts has been shown to undergo this type of reaction in the presence of EDTA and related chelating agents together with amines, thiosulphates and thiocyanates in highly alkaline solution.[15]

From these results it is obvious that the derivatisation by the direct addition of reagent to the sample, or, probably the direct injection of sample onto the column with derivatising agent in the mobile-phase as has been frequently employed,[16-18] is appropriate for the analysis of PM salts when EDTA or related complexing agents are present in the sample.

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