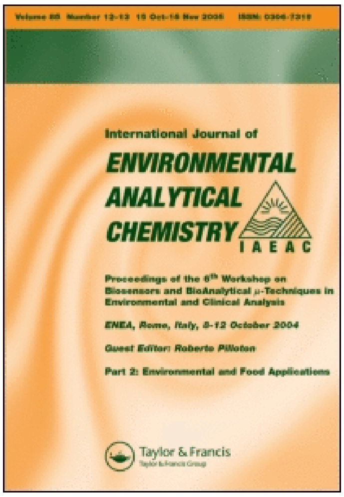

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Phenylmercury, Methylmercury and Inorganic Mercury in Potable and Surface Waters

J. Stary[a]; B. Havlík[ab]; J. Prášilová[a]; K. Kratzer[a]; J. Hanušová[ab]
[a] Department of Nuclear Chemistry, Czech Technical University, Břehová, Czechoslovakia [b] Institute of Hygiene and Epidemiology, Šrobárova, Czechoslovakia

To cite this Article Stary, J. , Havlík, B. , Prášilová, J. , Kratzer, K. and Hanušová, J.(1978) 'Determination of Phenylmercury, Methylmercury and Inorganic Mercury in Potable and Surface Waters', International Journal of Environmental Analytical Chemistry, 5: 2, 89 — 94

To link to this Article: DOI: 10.1080/03067317808071134

URL: http://dx.doi.org/10.1080/03067317808071134

Intern. J. Environ. Anal. Chem., 1978, Vol. 5, pp. 89–94

Printed in Great Britain

Determination of Phenylmercury, Methylmercury and Inorganic Mercury in Potable and Surface Waters

J. STARÝ, B. HAVLÍK†, J. PRÁŠILOVÁ, K. KRATZER
and J. HANUŠOVÁ†

Department of Nuclear Chemistry, Czech Technical University, Praha 1, Břehová 7 (Czechoslovakia)

(*Received April 29, 1977*)

Extraction chromatography and dithizone extraction were found to be the most promising methods to preconcentrate phenylmercury, methylmercury and inorganic mercury from 100–500 ml aqueous samples. By this manner the sensitivity of previously developed radioanalytical methods was increased down to 0.01 p.p.b. A number of potable and river water samples, beer, wine, fruit juices etc. have been analysed for their content of individual mercury species.

KEY WORDS: Trace analysis, radioanalytical methods, dithizone, phenylmercury, methylmercury, inorganic mercury, natural waters.

INTRODUCTION

In our previous papers very selective radiochemical determination of highly toxic phenylmercury[1,2] and methylmercury[3,4] has been described. These analytical methods are based on the isotope exchange reactions with the excess of inorganic mercury-203 or on the exchange reactions between phenylmercury and methylmercury chloride in the organic phase and sodium iodide-131 in the aqueous phase.

The preliminary experiments have shown that the sensitivity of the methods developed (0.5–1 p.p.b. in 5-ml sample) is not sufficient to determine organomercurials in natural waters. For this reason various separation techniques have been investigated in order to preconcentrate phenylmercury, methylmercury and inorganic mercury from 100–500 ml samples of potable

---

†Institute of Hygiene and Epidemiology, Praha 10, Šrobárova 48 (Czechoslovakia).

and river waters. Extraction chromatography and dithizone extraction were found to be the most promising methods for the concentration of organomercurials in the concentration range 0.01–2 p.p.b. The choice of the best organic solvent for various separation methods has been carried out from liquid–liquid distribution data of methylmercury and phenylmercury species.[5]

For the preconcentration of inorganic mercury the dithizone extraction method[6,7] has been adapted for our purpose.

EXPERIMENTAL

Apparatus and equipment

The scintillation counter with the well-type NaI(Tl) crystal was used for the radioactivity measurements.

Mercury Vapour Meter (Hendrey) was applied for the inorganic mercury determination by the method of cold vapour atomic absorption spectrophotometry.

Extraction column was prepared as follows: Dry polyurethane foam in the form of a cylinder (diameter 15 mm, length 60 mm) was packed into the chromatographic column (I.D. 10 mm, length 80 mm) with a 100-ml liquid reservoir applying a gentle pressure with a glass rod. Two millilitres of xylene was pipetted into the column, followed by 10 ml of 1 M hydrochloric acid. The excess of xylene was removed from the column by suction with a syringe.

Reagents

Unless otherwise stated, all reagents were of analytical reagent grade purity.

Buffer-masking solution was prepared by the dissolution of 7.5 g of disodium salt of ethylenediaminetetraacetic acid, 20 g of sodium hydroxide and 57.2 ml of glacial acetic acid in 1000 ml of bidistilled water.

2×10^{-5} M Dithizone solution in distilled chloroform or isooctane.

Alcaline solution of tin chloride was prepared by the dissolution of 1 g of stanneous chloride in 100 g of 30% sodium hydroxide.

Solution of mercury-203 chloride (Swierk, Poland) or mercury-203 acetate (Amersham, England) were made 1 M in hydrochloric acid and purified by the extraction with several portions of benzene. The solutions were diluted to the appropriate concentration with 0.5 M sulphuric acid (specific activity 100–500 mCi/g Hg). Carrier-free sodium iodide-131 (Dresden, GDR; Amersham, England) in 0.01 M sodium hydroxide was used for labelling 2×10^{-5} M sodium iodide in 1% ascorbic acid (specific activity 1000–2000 mCi/g I). The stock solution was purified before each set of experiments by the extraction with several portions of benzene.

Phenylmercury and methylmercury hydroxides were labelled with mercury-203 using isotope exchange method.[5]

Determination of phenylmercury

Extraction chromatography (Procedure A) 100 ml of the aqueous sample is acidified with 10 ml of conc. hydrochloric acid. Thus prepared solution is transferred immediately (phenylmercury chloride is partially decomposed by prolonged standing in acid solutions) into the liquid reservoir of the chromatographic column containing polyurethane foam loaded with xylene. Using the flow rate of about 5 ml/min, more than 97% of phenylmercury chloride is retained in the column. The column is washed by 10 ml of distilled water and phenylmercury is eluted from the column with 10 ml of 0.05 M potassium hydroxide. After the addition of 0.2 ml of conc. sulphuric acid, 0.2 ml of 2 M silver nitrate and 0.5 ml of 10^{-5} M mercury-203 sulphate, the mixture is kept standing at room temperature for 10 min. Then 2.0 ml of conc. hydrochloric acid and 5.0 ml of benzene are added and the mixture shaken for 1 min to transfer phenylmercury chloride into the organic phase. 3.0 ml of the centrifuged organic extract are measured using NaI(Tl) scintillation crystal. The total yield of the separation procedure described (75 ± 5%) was determined using labelled phenylmercury chloride added to potable and river waters. Inorganic mercury is not retained in the extraction column. In spite that methylmercury chloride is partially extracted into xylene and eluted by potassium hydroxide, it does not interfere in the determination.[2]

Dithizone extraction (Procedure B) 50 ml of buffer-masking solution are added to a 500-ml aqueous sample in a 1000-ml separation vessel and the prepared solution is shaken for 4 min with 50 ml of 2×10^{-5} M dithizone solution in isooctane. The separated organic phase is shaken for 2 min with a mixture of 9.5 ml of 0.5 M sulphuric acid and 0.5 ml of 2 M silver nitrate. To the separated aqueous phase, containing phenylmercury cations, 0.5 ml of 10^{-5} M mercury-203 sulphate is added and the mixture is kept standing for 10 min. The subsequent procedure is the same as described above.

The total yield of the separation of phenylmercury is about 70%. The calibration curve using synthetic samples is linear in the range 0.01–0.20 p.p.b. of phenylmercury chloride. Methylmercury and inorganic mercury, which are also completely extracted into dithizone solutions, do not interfere in the determination even if present in a great excess.[2]

Determination of both phenylmercury and methylmercury

Benzene extraction (Procedure C) 10 ml of conc. hydrochloric acid are added to a 100-ml aqueous sample. This solution is immediately shaken with 10.0 ml of benzene for 2 min. 4 ml of the separated organic phase are transferred into a test tube containing 0.2–0.5 ml of 2×10^{-5} M sodium iodide-131 in 1% ascorbic acid. After 1 min of shaking 3.0 ml of the separated organic phase was measured using NaI(Tl) scintillation crystal. Under the above conditions about 90% of phenylmercury and 50% of methylmercury are transferred into the organic phase.

Dithizone extraction (Procedure D) The extraction and back-extraction steps are identical with those described in Procedure B. To the separated aqueous phase, containing both phenylmercury and methylmercury cations, 1 ml of conc. hydrochloric acid and 5 ml of benzene are added. After 2 min of shaking 4 ml of the separated organic phase are treated as described under Procedure C.

Using labelled phenylmercury and methylmercury chlorides (0.05–0.5 p.p.b.) it has been found that the total separation yield for both species is about 70%. The calibration curve for synthetic samples was linear in the concentration range 0.02–0.20 p.p.b.

Determination of inorganic mercury

Dithizone extraction (Procedure E) 50 ml of buffer-masking solution are added to a 500-ml aqueous sample and the prepared solution is shaken for 4 min with two portions (30 ml and 20 ml) of 2×10^{-5} M dithizone in chloroform. Under these conditions more than 98–99% of mercury(II), methylmercury and phenylmercury are transferred into the organic phase. The separated organic phase is shaken for 5 min with 4.5 ml of a mixture of 0.2 M hydrochloric acid and 0.5 M sulphuric acid to which 0.5 ml of 5% sodium nitrite solution was added. Inorganic mercury(II) is transferred into the aqueous phase (total yield about 95%), whereas more than 99% of methylmercury and phenylmercury remain as chlorides in the organic phase. Aqueous phase was filtered (Schleicher Schuell 8714; white strip) and added into Mercury Vapour Meter. Immediately 2 ml of alcaline tin chloride solution and 2–3 drops of n-octanol (to prevent foam formation) are added. The calibration curve was constructed under the same conditions as for the analysed samples.

Using carbon tetrachloride as organic solvent the quantitative extraction of inorganic mercury(II), methylmercury and phenylmercury takes place. Under the above conditions about 10% of methylmercury and 3% of phenylmercury is transferred into the aqueous phase due to the lower distribution ratio of methylmercury and phenylmercury chlorides between carbon tetrachloride and aqueous phase.[5]

RESULTS AND DISCUSSION

Samples of potable water taken during winter period 1976–77 in water plants in Podolí and Jesenice near Prague, tap water from different parts of Prague as well as Vltava river water were analysed for their content of phenylmercury using Procedure A. It has been found that all samples analysed contained less than 0.05 p.p.b. of phenylmercury.

The analysis according to Procedure B, which is more sensitive, showed that the content of phenylmercury in Prague's potable water as well as in Vltava river water is lower than 0.01 p.p.b. Experiments with labelled phenylmercury have shown that gaseous chlorine or chlorine water quickly decomposes this compound to inorganic mercury. From this reason it can be expected that chlorinated potable water prepared from Vltava river water contain less than 0.001 p.p.b. of phenylmercury. Higher content of chlorine in potable water can destroy dithizone solution used for the preconcentration of phenylmercury. In that case the analysis can be started only after volatilation of gaseous chlorine.

From the results obtained it can be concluded that phenylmercury chloride, used as fungicide for dressing seeds in agriculture, does not pollute surface waters.

At the beginning the determination of both methylmercury and phenylmercury according to the very simple Procedure C has been carried out. It has been found that all samples of natural water contain less than 0.05 p.p.b. of organomercurials. This procedure has been also applied for the analysis of some sorts of Czech beer, wine, fruit juices, Coca-Cola, tea and coffee. In all cases the amount of organomercurials was lower than 0.1 p.p.b. On the other side the content of organomercurials found in chicken's liver was about 22 p.p.b.

The content of organomercurials in Vltava river water according to Procedure D is about 0.01–0.03 p.p.b.; potable water contains even lower amounts of organomercurials (methylmercury is also, but more slowly than phenylmercury, destroyed by gaseous chlorine).

The sensitivity of Hendrey's Mercury Vapour Meter (0.015 μg Hg in a 10-ml sample, i.e. 1.5 p.p.b.) was found insufficient for the direct determination of inorganic mercury in natural waters analysed. From this reason the preconcentration according to Procedure E has to be applied. It was found that the amount of inorganic mercury in Prague's tap water is lower than 0.1 p.p.b., however, in most samples analysed the concentration of inorganic mercury was lower than 0.02 p.p.b.

From the results obtained it is evident that the concentration of various forms of mercury in tap water is far lower than it is allowed according to Czechoslovak MPK (ČSN 830611, 1974: 0.001 mg Hg/l i.e. 1 p.p.b.). The content of mercury species in Prague's tap water is a little lower than those found by van der Sloot and Das (organic mercury 0.024 p.p.b., inorganic mercury 0.004 p.p.b.),[8] however, it is substantially lower than those found by Anand (total mercury content 0.7–8.6 p.p.b.).[9]

References

1. J. Starý and J. Prášilová, *Radiochem. Radioanal. Letters* **24,** 143 (1976).
2. J. Starý and J. Prášilová, *Radiochem. Radioanal. Letters* **26,** 33 (1976).

3. J. Starý and J. Prášilová, *Radiochem. Radioanal. Letters* **26**, 193 (1976).
4. J. Starý and J. Prášilová, *Radiochem. Radioanal. Letters* **27**, 51 (1976).
5. J. Starý and K. Kratzer, *Radiochem. Radioanal. Letters* **28**, 53 (1977).
6. J. Růžička and C. G. Lamm, *Talanta* **16**, 157 (1969).
7. M. Malát, Absorpční anorganická fotometrie, Academia, Prague 1973.
8. H. A. van der Sloot and H. A. Das, *Anal. Chim. Acta* **73**, 235 (1974).
9. S. J. S. Anand, *Radiochem. Radioanal. Letters* **27**, 43 (1976).