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DETERMINATION OF INORGANIC MERCURY BY GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

This paper details the study of a water-soluble trimethylsilyl derivative as a reagent for converting inorganic mercury to a methyl derivative thereby facilitating its measurement by gas–liquid chromatography. It is shown that the reagent is very stable, giving high efficiencies of conversion in strong acids at high temperatures. The quantitative nature of the reaction over the range 0.0025–10 ppm is given, and finally it is demonstrated how the reagent can be used to determine total mercury on wet oxidised fish sediment specimens.

INTRODUCTION

In a previous article[1] it was shown that inorganic mercury may be converted to a phenylmercury salt which on extraction could be detected and quantitated by gas–liquid chromatography. The reaction was found to be quantitative down to 0.05 ppm, close to the limit of detection of the instrument for that compound. The Peters reaction —the method employed— is widely used for large-scale preparation of organomercurials[2]. The reaction involves aryl- or alkylsulphinic acid salts, sodium benzenesulphinate being the one used in the above work.

It was thought feasible that the use of alkylsulphinates would convert inorganic mercury to alkylmercury salts giving a large increase in sensitivity together with easier chromatography. Unfortunately, the alkylsulphinates are not available commercially as yet and would have to be synthesised. Also they are less stable and more prone to oxidation than the corresponding aryl salts.

Recently an article published by De Simone[3] states that during a study on the chemical methylation of mercury by methylcobalamin (vitamin B_{12}) it was discovered that inorganic mercury salts are methylated in aqueous solution by trimethylsilyl salts commonly used as NMR reference compounds. This was considered worthy of investigation at the ppm level since the water-soluble trimethylsilyl derivatives are more stable than the sulphinic acid compounds.

The work carried out so far has given promising results and is presented in three parts:

(a) Preliminary investigation, which gives the general conditions needed for the reaction to proceed.

(b) Quantitative performance, which was checked over a wide range of concentration under the most ideal conditions.

(c) Application of reactions to environmental samples. The reactions were used to determine the total mercury content in some environmental samples the mercury concentrations of which were at a level of between 2–100 ppm.

PRELIMINARY INVESTIGATION

The two trimethylsilyl derivatives mentioned in De Simone's paper were: sodium 2,2′-dimethyl-2-silapentane-5-sulphonate (DSS) and sodium 3-trimethylsilyl-propionate (TSP). All the work in this study was on DSS, being the only one available in this country at the time. Both DSS and TSP can be obtained from Merck, Sharpe and Dome (Rahway, N.J., U.S.A.).

Interference peaks which arose from one batch of DSS were removed by a triple extraction of a 1% w/v aqueous solution with toluene.

The reactions were carried out in 25-ml ground-glass stoppered tubes. After the reaction conditions had been fulfilled, the solution was shaken with toluene and an aliquot was injected into a gas chromatograph to follow the yield of the methylmercury salt formed. Standard inorganic mercury solutions were made up from mercuric chloride in either distilled water or 1 *N* acid.

At near neutral pH and room temperature little reaction occurred at the level of 100 ppm and lower. The yield rapidly increased with a decrease in pH and an increase in temperature. Using 1 ppm inorganic mercury solutions, the biggest yields were obtained in 10 *N* H_2SO_4 kept at boiling point for at least 5 min. An attempted calibration from 0.1–1 ppm using the above conditions gave an 'S'-shaped curve with very low efficiency of conversion near the 0.1-ppm level. Clearly, these conditions were not favourable for quantitative work.

On further investigation, high yields and quantitative results were eventually achieved when the solution contained traces of nitrogen dioxide (formed by adding sodium nitrite). This probably has a catalytic effect.

Change in acid type also had an influence on the efficiency of the reaction. Sulphuric acid gave the highest followed closely by nitric acid, then trifluoroacetic acid, with hydrochloric acid giving very low yields. The stability of the DSS reagent was evident from the fact that the reaction proceeded smoothly in boiling 5 *N* nitric acid containing small amounts of nitrogen dioxide.

QUANTITATIVE PERFORMANCE

For quantitative work, particularly when dealing with components which may be at the picogram level, the gas–liquid chromatographic conditions are very important. The following set-up was found to be satisfactory for long-term operation.

A glass column, 150 cm long by 0.4 cm I.D., was packed with 80–100 mesh acid-washed Supasorb (BDH, Poole, Great Britain) with a loading of 5% w/w monoethylene glycol adipate polyester coated by the rotary evaporator technique. Long-term conditioning was essential for maximum sensitivity and optimum peak symmetry. The column was heated at 210° with argon as carrier gas (50 ml min^{-1}) for 48 h. The temperature was dropped to 190° for a further 24 h. The column was then used normally but left overnight at 190° for a further three days with nitrogen carrier gas (50 ml min^{-1}). During this period sensitivity and peak shape continued to improve as the bleed rate from the polyester decreased (see Fig. 1). The column thus conditioned could be used continuously for at least a month with little change in performance. Standby conditions when not in use were a temperature of 110° and a carrier gas flow-rate of 50 ml min^{-1}. The gas chromatograph was a Pye Series 104 one (Pye Unicam, Cambridge, Great Britain) fitted with a heated electron capture detector (ECD) containing a ^{63}Ni source. The normal operating conditions were: injection port temperature, 210°; column temperature, 160–175°; detector temperature, 250–275°; carrier gas (nitrogen) flow-rate, 100 ml min^{-1}; purge gas (nitrogen) flow-rate, 100 ml min^{-1}. The detector was supplied with pulsed d.c., with a pulse width of 150 or 50 μsec.

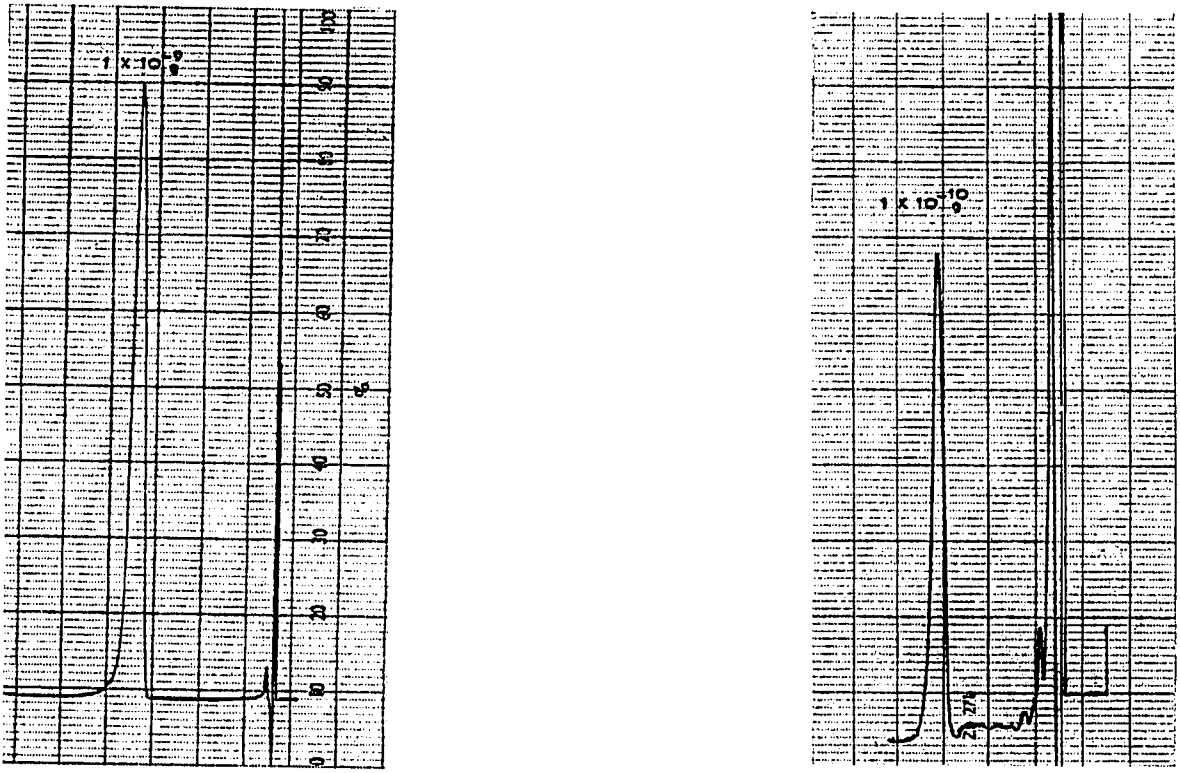

Fig. 1. Examples of column and detector performance using standard methylmercury chloride solutions in toluene.

For an assessment of the quantitative nature of the DSS reaction, sulphate media were used throughout. Four calibration series were attempted over the wide range of 0.0025–10 ppm.

Into a 25-ml tube with a B24 ground-glass neck were placed 5 *N* H_2SO_4 (10 ml),

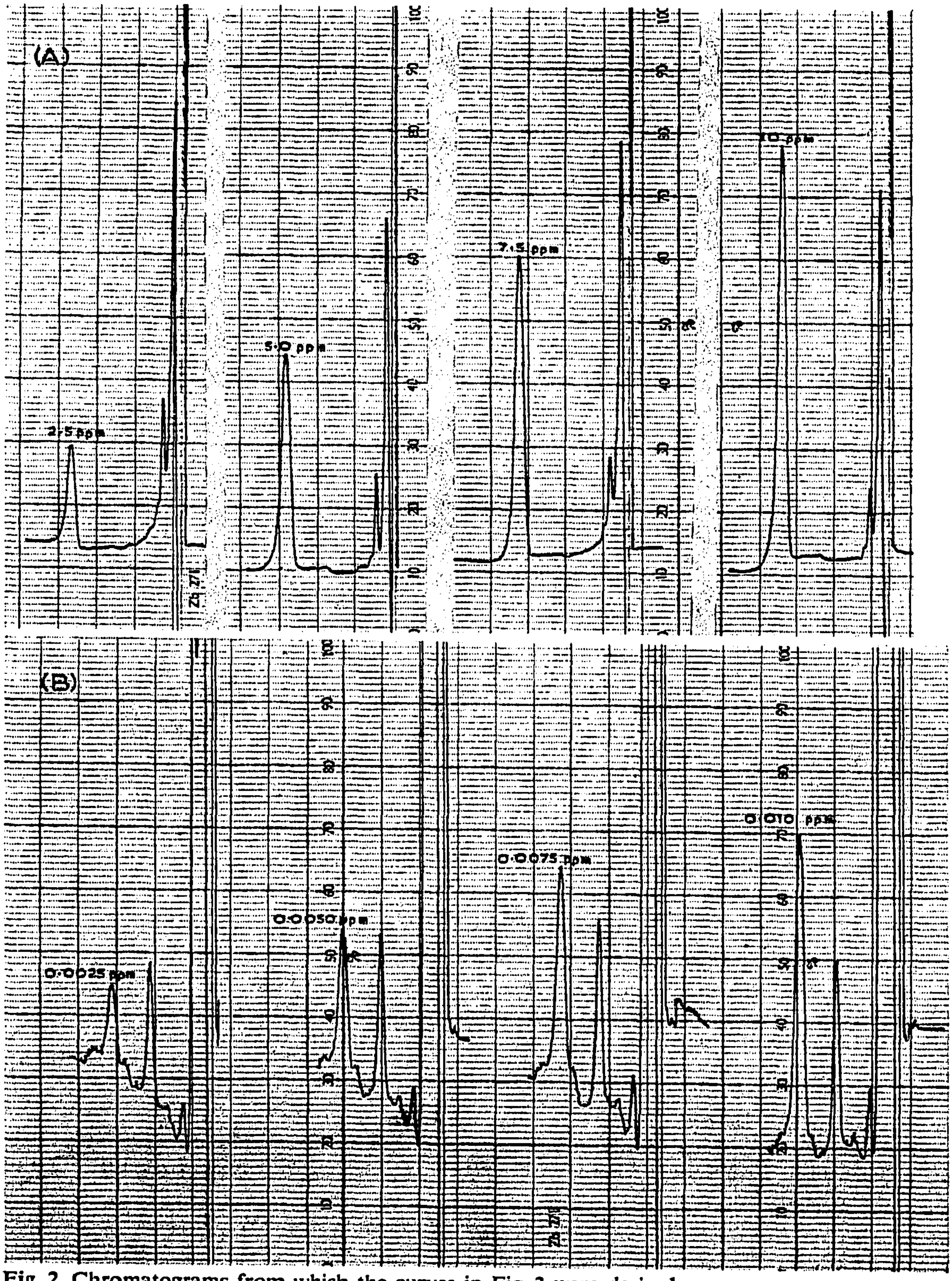

Fig. 2. Chromatograms from which the curves in Fig. 3 were derived.

standard inorganic mercury solution (2 ml), 15% w/v aqueous $NaNO_2$ solution (0.1 ml), and 1% w/v aqueous DSS (1 ml). This mixture was boiled to remove excess nitrogen dioxide, placed in a boiling water-bath for 10 min, cooled, and extracted with benzene (10 ml).

To keep within the linear range of the ECD (a maximum of 1 ng was injected), the more concentrated ranges were diluted before injection. For the 0.0025 to 0.010-ppm series interference peaks were removed by using a clean-up procedure similar to that used by Uthe *et al.*[4] for fish tissues.

A 5-ml aliquot of the benzene extract was extracted twice with 2-ml and 1-ml portions of 0.005 *M* sodium thiosulphate solution. To the combined extracts 3 *M* potassium iodide (1 ml) was added and the mixture was then shaken with toluene (5 ml). The methylmercuric iodide in the final extract is light sensitive and should be injected as soon as possible or kept light-tight.

The four ranges gave reasonably linear plots, passing through the origin; examples of the highest and lowest ranges are shown in Fig. 2 and the actual chromatograms from which they were derived are shown in Fig. 3.

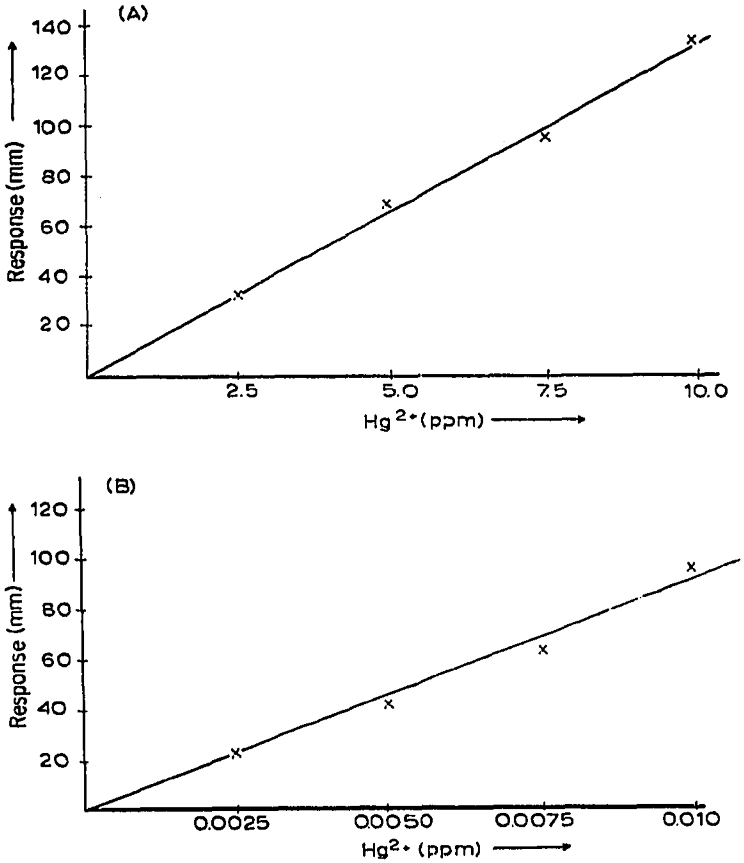

Fig. 3. Calibration series on inorganic mercury solutions in sulphate media. (A) 2.5–10 ppm and (B) 0.0025–0.010 ppm.

APPLICATION OF THE DSS REACTION TO ENVIRONMENTAL SAMPLES

To obtain mercury results on this type of sample a wet oxidation scheme is generally employed, usually nitric acid alone or in a mixture with other oxidising acids. The DSS reaction works well in nitric acid but the yield of methylmercury is not as high (70–80%) as in sulphate media (90–100%). The main inhibitors of the reaction were halides, particularly chloride. This was not a problem in the finalised procedure since halides are lost from boiling nitric acid solution.

Some fish and sediment samples were analysed which had already been the subject of an extensive round-robin programme.

Approximately 0.1-g portions of the samples (in duplicate) were weighed to nearest 0.001 g into 25-ml tubes to which were added concentrated HNO_3 (3.5 ml) and 15% w/v $NaNO_2$ (0.2 ml). The tube was heated gently until the reaction subsided (approx. 3 min) and then boiled for a further 5 min. When cool, distilled water (7 ml), more $NaNO_2$ (0.1 ml), and 1% w/v DSS (1 ml) were added. The tube contents were boiled for 3–4 min to expel the last traces of nitrogen dioxide and immersed in a boiling water-bath for 15 min. The cooled solution was shaken with benzene (10 ml), dried with Na_2SO_4, and then either injected directly into the gas chromatograph (with suitable dilution for concentrated solutions of methylmercury) or passed through the clean-up procedure if interfering peaks were present. Calibration series of standard inorganic mercury solutions were carried through the above procedure to check the linearity of response over the range of interest. Also one calibration control was run with each batch of unknowns.

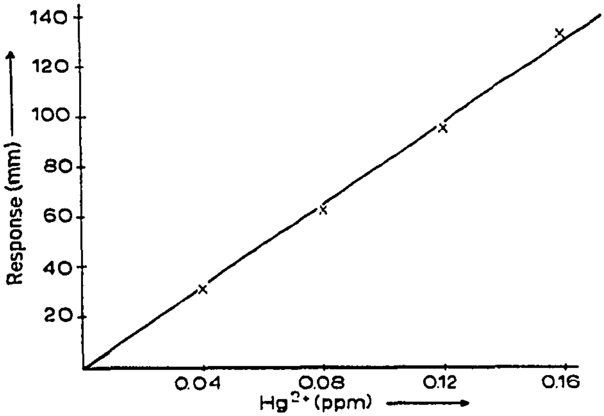

Fig. 4. Calibration graph of inorganic mercury standards in nitrate media as control for fish and sediment samples.

Fig. 4 depicts a calibration series from 0.04–0.16 ppm in the final extract. Fig. 5 shows the peaks derived from (A) E.P.A. sediment sample No. 72C-5644, diluted to a factor of five before injection, and without clean-up, and (B) E.P.A. fish sample No. 72C-1222, passed through a clean-up procedure. Table I gives the total-mercury results obtained by the DSS method and compares them with those from the

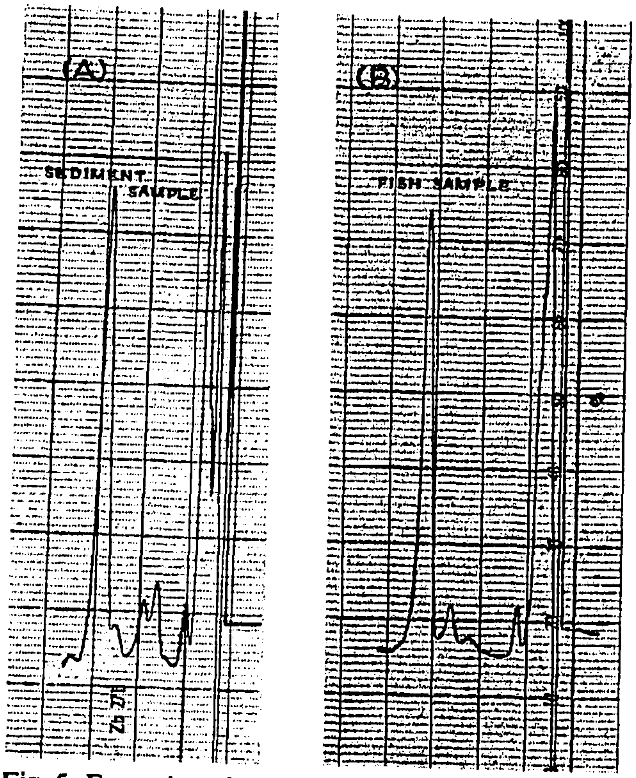

Fig. 5. Examples of peaks obtained for total mercury in (A) sediment sample without clean-up and (B) fish sample with clean-up procedure.

TABLE I

TOTAL MERCURY IN SEDIMENT AND FISH SAMPLES BY THE DSS REACTION

Matrix	*Sample no.*	*Results from the DSS reaction*		*Results from round-robin survey*		
				Mean	*Standard deviation*	*Number of analyses*
Sediment	72C-5644	44.0 47.0	45.5	44.1	9.13	138
	72C-5643	136 129	132	109.6	21.5	135
Fish	72C-1222	2.79 2.89	2.84	2.06	0.83	134
	72C-1224	8.58 8.53	8.56	7.23	2.02	133

round-robin survey, which used a variety of methods but mainly wet oxidation followed by cold vapour atomic absorption.

DISCUSSION AND CONCLUSION

It has been shown that the DSS reaction can give quantitative conversion of inorganic mercury to a methylmercury salt over the range 0.0025–10 ppm. The reagent is stable to strong acids containing mild oxidising agents. Chloride was found to seriously inhibit the reaction but can be removed by strong oxidising agents such as potassium persulphate and hot concentrated nitric acid. More work is needed to check other possible interferences, and standard addition procedures can be used for complex samples.

The reaction was attempted on some environmental samples and gave results which are higher than the means from the round-robin survey but within one standard deviation.

Modern electron capture detectors with pulsed d.c. supply are capable of very high sensitivity to organomercury compounds. The DSS reaction in conjunction with an efficient clean-up procedure should be capable of analysis down to the ppb range. Thus the gas–liquid chromatographic method could become a valuable alternative to other techniques, such as cold vapour atomic absorption, where special equipment is needed, and neutron-activation analysis, to which most analysts have relatively little access.

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