

CHROM. 6384

Note

The estimation of inorganic mercury (at low concentrations) by gas chromatography

In recent years the technique of gas chromatography (GC) has been applied to the study of metal ions in aqueous solution. The availability of highly sensitive and selective detectors such as the electron-capture detector could mean identification and estimation at very low concentrations. Since the requirements for good GC are reasonable volatility and thermal stability of the compound at the temperature of elution, most metal species have to be converted into such a form prior to analysis. Two possibilities are: (1) The formation of metal chelates. MOSHIER AND SIEVERS¹ describe how acetylacetone and more particularly its halogen derivatives can be used to form a number of metal chelates suitable for GC. This approach is used by ROSS AND SIEVERS², who show for example a method for the estimation of trace amounts of chromium in ferrous alloys by conversion to the trifluoroacetylacetone complex. (2) The formation of an alkyl or aryl metal bond. The number of metals to which this can be applied is limited because of the need for ease of formation combined with stability towards oxidation and hydrolysis.

It is well known (and indeed is the cause of some concern to the environment) that mercury forms a strong carbon-to-metal bond highly stable towards oxidation and hydrolysis. For the estimation of inorganic mercury the reaction chosen to convert to the organometallic form should be quantitative or near quantitative with reproducible yields. The subject of this article concerns an investigation of the PETERS' reaction³ and its application to the analysis of low concentrations of inorganic mercury. The reaction between mercuric chloride and sulphinic acids



has been widely used for the synthesis of organomercury salts. Initially used for the aromatic series of mercury salts it may now also be used for the synthesis of mercury containing aliphatic and heterocyclic compounds and metallocenes⁴. Because the aromatic sulphinic acids are the most stable, and readily available, it was decided to convert the inorganic mercury to a phenylmercury salt using sodium benzene sulphinate. The solution is then extracted for injection into a gas chromatograph. The GC of organomercury compounds is well established and is given comprehensive coverage in a review article by FISHBEIN⁵.

Experimental

Reaction conditions. The basic procedure is straightforward. It involves boiling a weak acid solution of the mercury with a small amount of sodium benzene sulphinate for a short period. When cool, the phenylmercury is ready for extraction. The volumes employed depended on the mercury concentration, larger volumes being chosen for the more dilute solutions so that measurable peaks would be

obtained after extraction. For example, the procedure for the 0.05–0.2 p.p.m. range of mercury was as follows: 5 ml of a 2% aqueous solution of sodium benzene sulphinate and 5 ml of 4 *N* acetic acid were added to 100 ml of the mercury solution diluted from standards. This mixture was brought to near boiling for 5 min and cooled to room temperature ready for solvent extraction.

Extraction conditions. The solution obtained above was subjected to an extraction procedure similar to that used by WESTOO^{6,7} for the investigation of methylmercury in biological material. This was found to work equally well with phenylmercury salts and was used primarily to prevent sulphur compounds from being injected into the GC system. The following procedure was employed: The cooled solution was made approximately 1 *N* with conc. HCl and shaken with an equal volume of toluene for 3 min. The aqueous layer was run off and the toluene washed twice by gentle rotation with distilled water. 6.0 ml of a cysteine acetate solution (1.00 g cysteine hydrochloride (1 H₂O), 0.775 g sodium acetate (3 H₂O) and 12.5 g anhydrous sodium sulphate made up to 100 ml with water) was added and shaken for 3 min. The cysteine acetate layer was run into another separating funnel and 2.0 ml of 6 *N* HCl and 10.0 ml of toluene were added. The final solution was shaken for a further 3 min, the toluene layer decanted off and a suitable aliquot injected into the gas chromatograph.

GLC conditions. All results were obtained on a Pye 104 gas chromatograph fitted with a heated electron capture detector with variable pulsed d.c. supply. The column was 0.5 m × 3 mm I.D. packed with 5% ethylene glycol adipate polyester on Supasorb (a.w.). The operating parameters were: column temperature, 185°; detector temperature, 280°; injection port temperature, 230°; carrier gas (argon) flow-rate, 120 ml/min; pulse space, 500 μsec; chart speed, 8 in./h; volumes injected, between 1 and 4 μl; with the above conditions, the detection limit for phenylmercuric chloride is approximately 2 × 10⁻¹⁰ g.

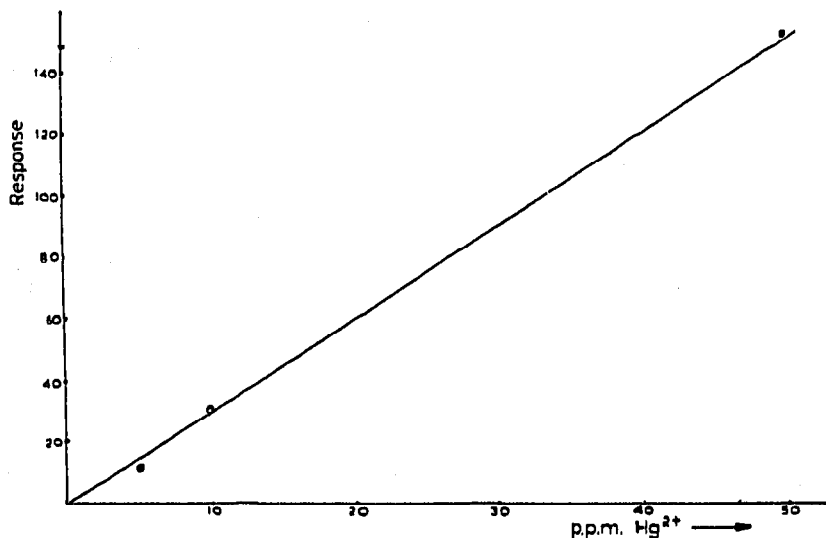


Fig. 1. Calibration series 5–50 p.p.m. Hg²⁺. Volume of aqueous, 10 ml; volume of final extract 10 ml; volume of injection, 1 μl.

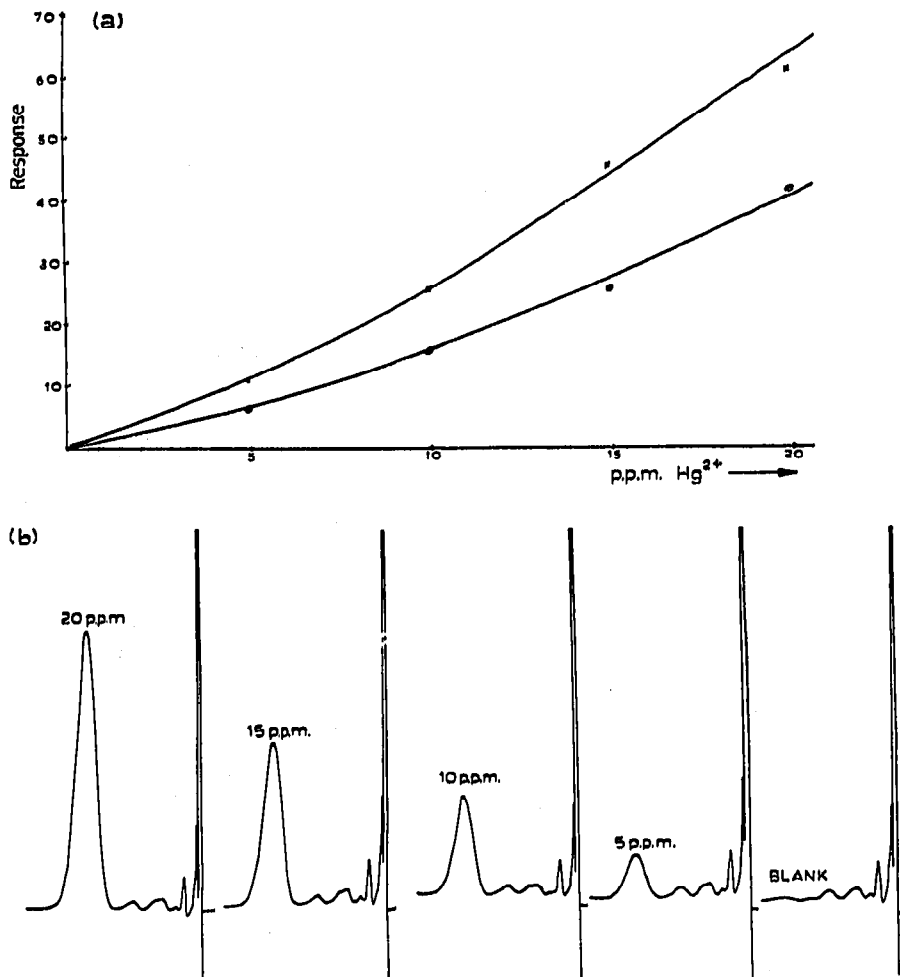


Fig. 2. (a) Calibration series 5-20 p.p.m. Hg^{2+} . Volumes as in Fig. 1. \times = Phenylmercuric chloride standards 5-20 ng for comparison. (b) The GC traces obtained from injection of the final extracts for the series 5-20 p.p.m. shown in (a).

Results

The results are expressed as p.p.m. of inorganic mercury (Hg^{2+}) in the solution before conversion to a phenylmercury salt. The first calibration (Fig. 1) gave some idea of linearity from 5-50 p.p.m. Since this looked promising, more precise and careful calibrations were carried out. The range from 5-20 p.p.m. is shown in Fig. 2 a. Comparison with phenylmercuric chloride standards (5-20 ng) indicates that the curvature was not due to PETERS' reaction. The gas chromatographic traces from which the above calibration is derived are shown in Fig. 2b. Finally, Figs. 3 and 4 give the concentration ranges 0.5-2.0 p.p.m. and 0.05-0.20 p.p.m., respectively. Results for lower concentration cannot be obtained at present because of close proximity to the limit of detection for phenylmercury salts (phenylmercuric chloride, acetate and nitrate all give identical retention times).

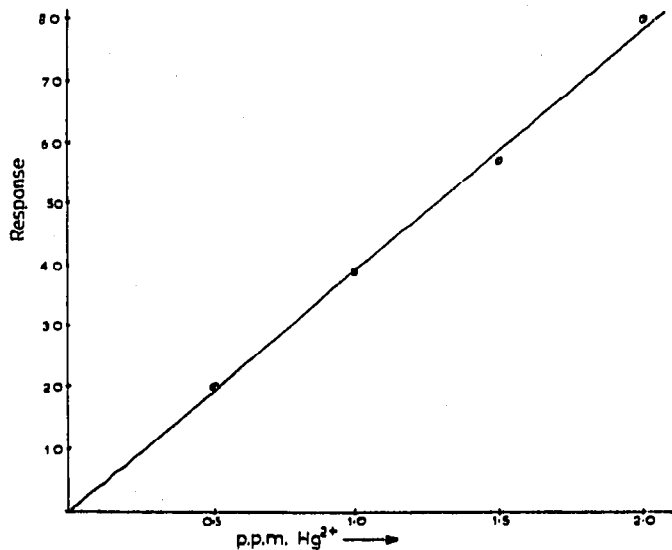


Fig. 3. Calibration series 0.5–2.0 p.p.m. Hg^{2+} . Volume of aqueous, 20 ml; volume of final extract, 10 ml; volume of injection, 1 μ l.

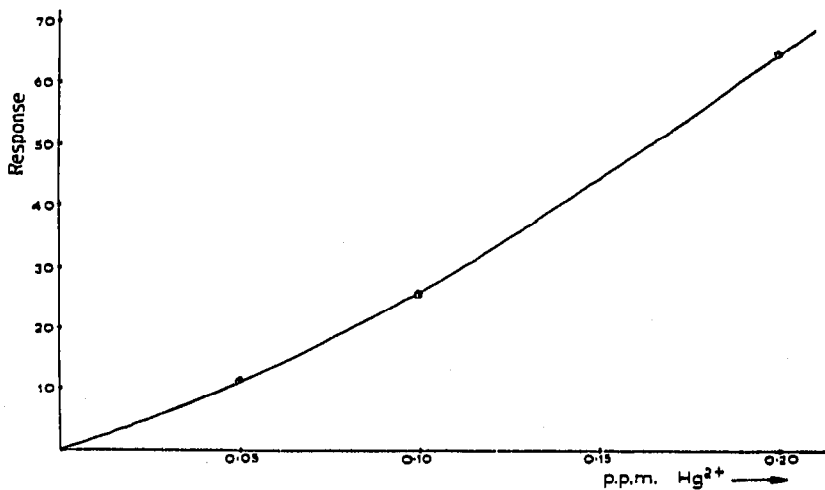


Fig. 4. Calibration series 0.05–0.20 p.p.m. Volume of aqueous, 100 ml; volume of final extract 5 ml; volume of injection, 4 μ l.

Conclusion

The above results show the quantitative nature of PETERS' reaction over three orders of magnitude 0.05–50 p.p.m. The reaction was found to proceed smoothly only in weak acid solution in the absence of oxidising agents. If the excess benzene sulphinate can be destroyed after boiling, the WESTOO procedure may be substituted for a single extraction, though the effect of relatively large amounts of benzene sulphinate on column life has not yet been ascertained.

Lower concentrations of inorganic mercury may be investigated if converted

to an alkylmercury salt. The reason being the much lower detection limits (approx. $\times 10$) when compared with the corresponding aryl salts. This reaction is at present under active investigation.

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