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Determination of Tin in Environmental  
Samples by Hydride Generation

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## EXECUTIVE SUMMARY

Tin can be determined simultaneously with arsenic and selenium or it can be determined separately under conditions that give the maximum sensitivity for tin. It has been determined that when tin is measured separately there is an increase in sensitivity of about a factor of 10. The preservation system used to preserve samples for arsenic and selenium and the preservation system used for the other trace metals have been shown to both be effective in preserving tin in water samples.

# ABSTRACT

The optimum condtions for producing stannane are in a matrix of 0.2 N.  $\text{HNO}_3$ . Preservation of tin in water samples can be achieved by the addition of either 0.2% W/V  $\text{HNO}_3$  or 0.2% W/V  $\text{H}_2\text{SO}_4$ . The decomposition of organo -- tins before the determination of total tin by hydride generation is most conveniently carried out by oxidation with potassium persulfate.

## RÉSUMÉ ADMINISTRATIF

On peut doser simultanément l'étain, l'arsenic et le sélénium, ou encore réaliser le dosage séparément dans des conditions de sensibilité maximale pour l'étain. Il a été établi qu'il y a accroissement de la sensibilité par un facteur d'environ 10 lorsque le dosage de l'étain se fait séparément. Le système utilisé pour conserver l'arsenic et le sélénium dans les échantillons et les systèmes semblables utilisés pour conserver les autres métaux traces permettent de conserver l'étain dans des échantillons d'eau.

## RÉSUMÉ

Une matrice composée de  $\text{HNO}_3$  0,2 N constitue le milieu optimal pour produire du stannane. On peut conserver l'étain dans les échantillons d'eau en ajoutant 0,2 % (masse/volume) de  $\text{HNO}_3$  ou 0,2 % (masse/volume) de  $\text{H}_2\text{SO}_4$ . L'oxydation avec du persulfate de potassium constitue une méthode très efficace pour décomposer les composés organiques de l'étain avant le dosage de l'étain total par production d'un hydrure.

## INTRODUCTION

The determination of tin by hydride formation with spectrometric detection in both continuous and batch systems is described by several authors (1-4). In general, the emphasis has been on the establishment of compromise conditions that will allow several of the hydride-forming elements, As, Se, Sb, Bi, Te, Ge, Sn, and Pb to be determined simultaneously. This is particularly true when an Inductively Coupled Argon Plasma system (ICAP) is used as the detector. In many environmental applications the elements of greatest interest have been arsenic and selenium. Because selenium occurs at very low levels and has a poor sensitivity in the detection step, in our laboratories the hydride-forming step is carried out in a 4N HCl matrix, providing the conditions optimum for this element. This allows a simultaneous determination of arsenic, selenium and tin (also antimony and bismuth) but the sensitivity of tin is much reduced. There is increasing interest in the environmental effects of tin and in this work the hydride-generation step has been studied in order to establish the optimum conditions for the determination of tin in water, fish and sediments. It is found that using a matrix of 0.2N HNO<sub>3</sub> the sensitivity for tin is increased by about a factor of 10 over the matrix of 4N HCl. Studies have also been made of preservation techniques for water samples and procedures for the destruction of organo-tins.

## EXPERIMENTAL

### Apparatus and Reagents

These are as previously described (5).

### Procedure

Water Samples: To 50 mL water, that has been preserved by the addition of 0.2% v/v  $\text{HNO}_3$ , is added 3.5 mL 4% potassium persulfate solution. The solution is boiled gently for 30 minutes, cooled and the volume made up to 50 mL. The samples are run through the automated hydride generator system using a wash solution of 0.2%  $\text{HNO}_3$  in water.

Fish samples: The samples are treated by a nitric-sulfuric acid digestion as previously described(6). Twenty mL of the diluted digest solution is taken and neutralized to a pH of approximately 7 with 20% NaOH solution. 0.1 mL nitric acid (70%) is added and the solution volume is made up to 50 mL.

Sediments: The sample is fused with sodium hydroxide as previously described (5). The crucible is cooled and the contents are dissolved in 50 mL 0.2  $\text{HNO}_3$ . The solution is allowed to stand to permit any precipitated silicic acid to settle and the solution is decanted into the sampler tubes.

## RESULTS AND DISCUSSION

### Method Optimization

It has previously been reported that stannane production is dependent on the matrix acid concentration and in hydrochloric acid the maximum occurs in a narrow range about 0.1 N (1,7,8). Organic acids such as tartaric acid, have also been used as the matrix (3,8). In the present work, it was found that nitric acid was a better matrix than HCl since the maximum production of stannane occurred over a broader concentration range. This is shown in Figure 1. Nitric acid is preferred over the organic acids as it is virtually tin-free and it has been reported (3,8) and confirmed in the present work, that organic acids generally contain high levels of tin with a consequent increase in the 'blank' value for the determination.

The effect of borohydride concentration on stannane production was determined and is shown in Figure 2. This is a similar relationship to that previously reported (2) and is also similar to that seen in the production of hydrogen selenide and arsine in 4N HCl (9).



### Detection Limits

The detection limites were calculated as previously described (5) in the work on arsenic and selenium. In an unconcentrated sample the detection limit is  $0.02 \mu\text{g L}^{-1} \text{ Sn}$ .

### Organo-Tins

Organo-tins can be reduced by borohydride to the corresponding hydrides and this forms the basis for their direct determination. Hodge *et al.* (10) reduced the tin compounds in natural waters with sodium borohydride, collected the hydrides in a liquid nitrogen-cooled trap and selectively vaporized them into a furnace in an atomic absorption spectrophotometer. In the present work, it was found that the methyl tins, ( $\text{MeSnCl}_3$ ,  $\text{Me}_2\text{SnCl}_2$  and  $\text{Me}_3\text{SnCl}$ ) would react to form hydrides in the manifold and were indistinguishable from inorganic tin. The higher molecular weight organo-tins such as tributyl tin chloride, however, gave hydrides that had different characteristics. These hydrides gave a delayed response to the ICAP detection and had very long wash-out times, presumably because of their lower volatility relative to stannane. Hence, it was concluded that to determine total tin, i.e. both inorganic and organic tin, it is necessary to first convert all the tin to a common inorganic form. It was found that treating the sample with persulfate gave complete recovery of the methyl and butyl tins. (It was confirmed that the procedure used in

the selenium analysis (5) of boiling with persulfate-HCl also gave complete recovery of these organotins).

#### Water Sample Preservation

Water samples taken for trace metal analysis in these laboratories are preserved by the addition of 0.2% v/v nitric acid. Samples for the determination of arsenic and selenium are preserved with 0.2% v/v sulfuric acid. These two preservative systems were investigated at a level of  $10 \mu\text{g L}^{-1}$  tin and both were found to preserve the tin level for at least 30 days.

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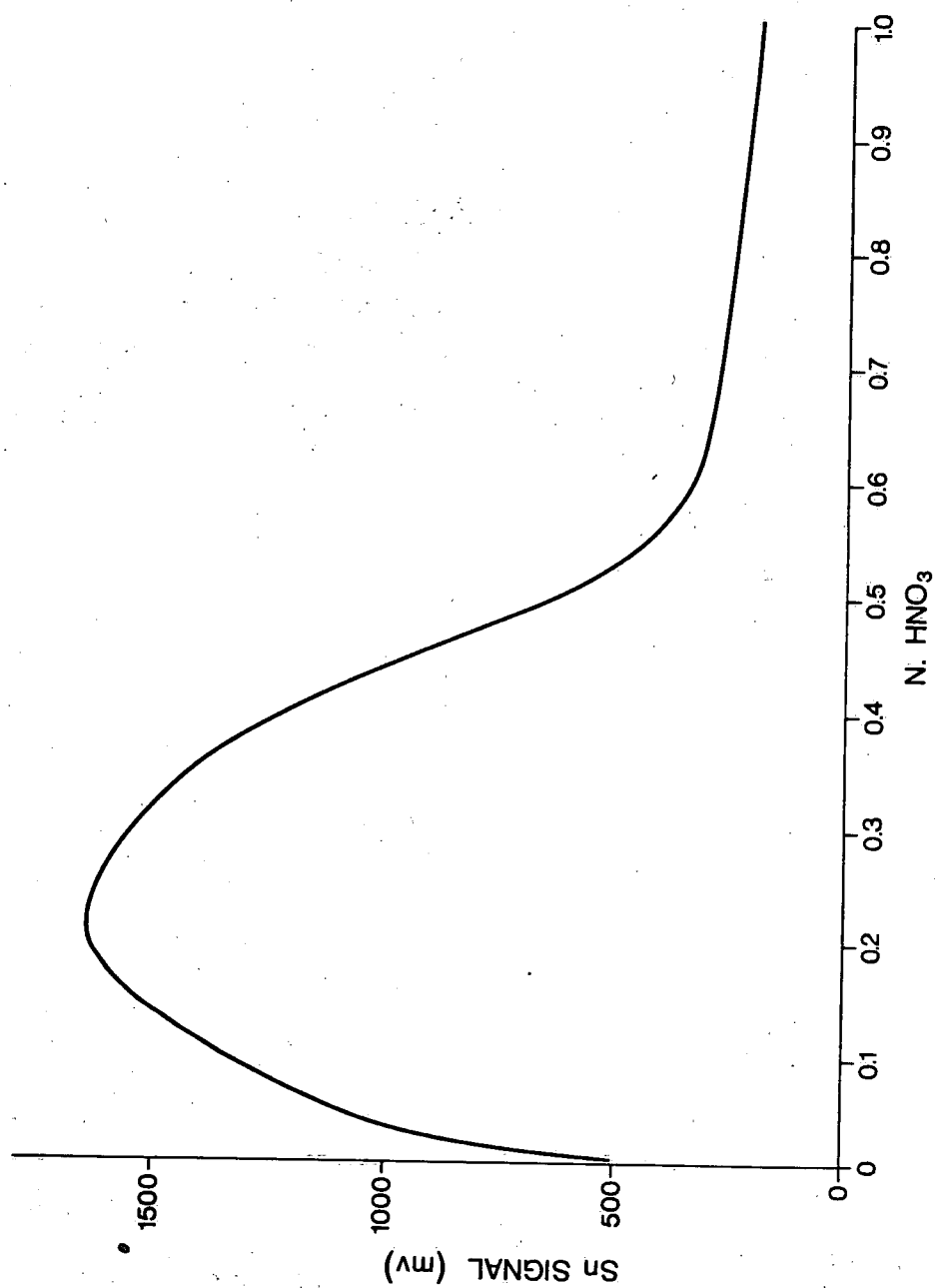


Figure 1 Effect of Nitric Acid concentration on Stannane production

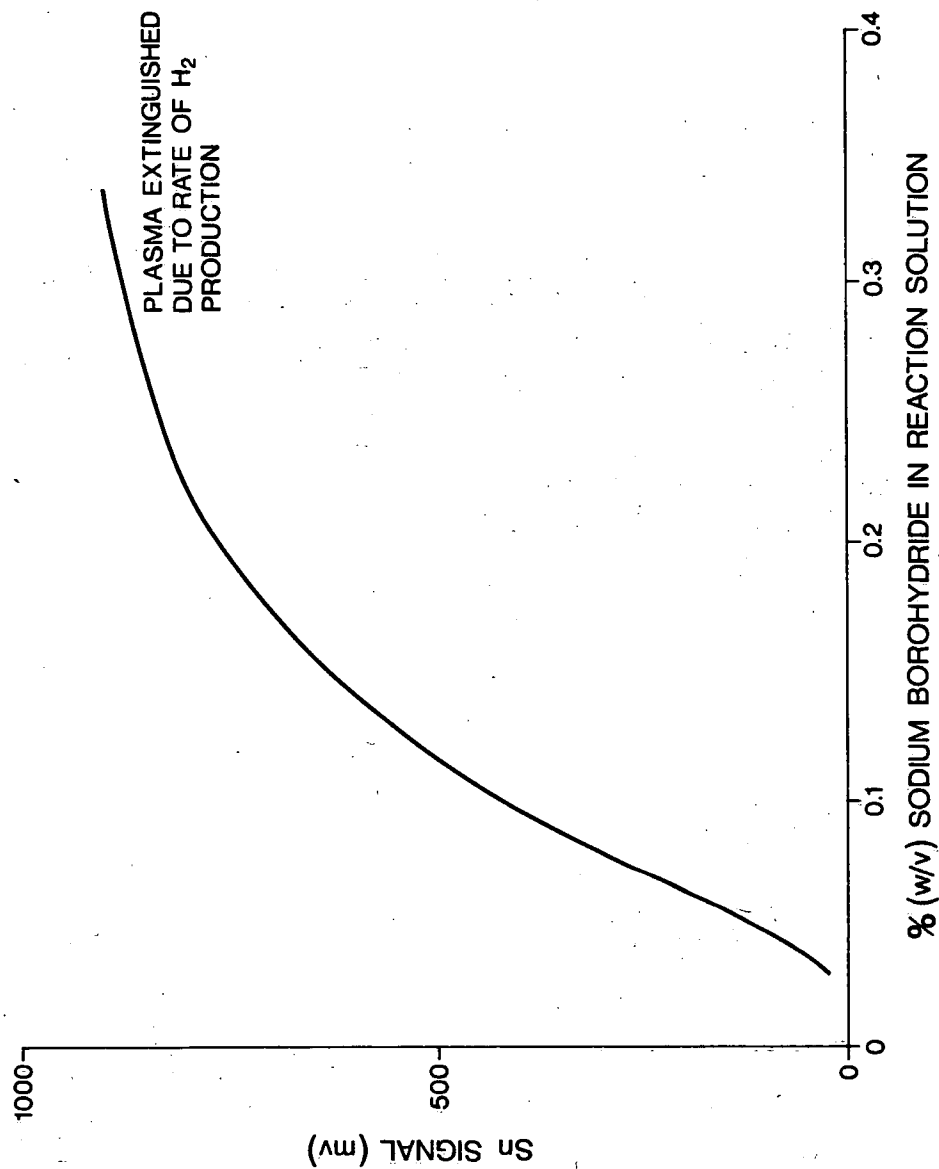


Figure 2 Effect of Borohydride concentration on Stannane production

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