PREPARATION OF $^{113}Sn^{2+}$ AND $^{113}Sn^{4+}$ COMPOUNDS.

Richard A. Hiles

The Procter & Gamble Company
Miami·Valley Laboratories
P.O. Box 39175
Cincinnati, Ohio 45239

SUMMARY

A need for valence-pure $^{113}Sn^{2+}$ and $^{113}Sn^{4+}$ compounds required the development of the methods reported in this communication. Commercially available ^{113}Sn comes either as metallic Sn which is contaminated with isotopes of Sn as well as with antimony and indium or as a hydrochloric acid solution of $^{113}SnCl_4$ plus some $^{113}SnCl_2$. The procedures reported here yield a chemically stable powder of $^{113}SnSO_4$ which is greater than 98% in the Sn^{2+} form.

There are two major advantages in preparing the $^{113}SnSO_4$. First, many other $^{113}Sn^{4+}$ compounds can be readily prepared by oxidizing an acidic solution of $^{113}SnSO_4$ with hydrogen peroxide with no contamination of the resulting Sn^{4+} solution with oxidizing agent. In contrast, the reduction of Sn^{4+} to Sn^{2+} salts is not easily accomplished. Second as polarographic evidence indicates, sulfate is a very weak complexer of Sn and thus many new salts of Sn can be prepared simply by mixing a selected new anion into a solution containing $^{113}SnSO_4$.

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EXPERIMENTAL

Preparation of ^{113}SnSO$_4$

Radioactive Sn in 2N HCl was purchased from New England Nuclear Co. The desired amount of activity was added to a solution containing 10 mg of carrier SnSO$_4$ in 1 to 2 ml of 6N HCl.* In a nitrogen box the solution was heated in a boiling water bath, and 12 mg of aluminum foil in $\sim$ 2 mg pieces was added. Each piece of foil and any precipitated tin were allowed to dissolve before the next piece was added.

A solution of SnSO$_4$ was prepared by an adaptation of the procedure of Donaldson and Moser (1); air-free solvents were used under a nitrogen atmosphere.

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*It was found most convenient to use a tall polyethylene vial in order to avoid spattering losses during the reduction.

To 7.7 ml of water and 0.39 ml of H$_2$SO$_4$, 950 mg of CuSO$_4$ was added. The solution was heated to 80° and 950 mg of purified Sn (200 mesh) was added. The mixture was boiled and stirred until the blue color disappeared. The precipitates were removed by filtration and the ^{113}Sn^{2+} as prepared in the preceding paragraph added to the filtrate. Crystals of ^{113}SnSO$_4$ were formed when the solution was evaporated to a slurry under reduced pressure. The crystals were collected by filtration and rinsed with absolute ethanol followed by diethyl ether. The yield was usually 400 mg of ^{113}SnSO$_4$ in a 66% radiochemical yield.

Titration to the potentiometric endpoint with KIO$_4$ showed that all preparations were > 98% in the Sn^{2+} form. The powder was chemically stable when stored under nitrogen in the dark (1). Analysis by atomic absorption spectroscopy indicated a contamination of 2.8 µg Cu per gram of SnSO$_4$.

Preparation of ^{113}Sn(SO$_4$)$_2$ Solutions

Radioactive Sn^{4+} solutions were prepared by oxidation of Sn^{2+} with 30% H$_2$O$_2$. Since oxidation with H$_2$O$_2$ causes an increase in alkalinity, it was necessary to have sufficient acid present to inhibit the formation of tin hydroxides. Oxidation was carried out to the potentiometric endpoint to prevent contamination from excess oxidant.

Preparation of Other Anionic Forms of ^{113}Sn

Although much data exist on Sn complexation (2), the eccentricities of Sn electrochemistry make direct comparison of published association constants extremely liable to error.

Therefore, the positions of the $E_{1/2}$ of several Sn compounds were determined under identical conditions, and the $\Delta E_{1/2}$ as compared to $Sn(ClO_4)_2$ used as a rough indication of relative complexing strength (Table 1). Without additional information, the values of the stability indeces cannot be used to determine complex composition or strength and, therefore, no absolute quantitative conclusions can be made from them. However, one can see from the data that sulfate binds Sn very weakly and that other complexes of Sn can be prepared by simply mixing a selected new anion into a solution of $^{113}SnSO_4$.

ACKNOWLEDGMENT

Table 1. Polarographic Stability Indexes
For Sn^{2+} Complexes[a]

Complexer	Molar Ratio of Complexer to Tin	pH	Stability Index ($\Delta E_{1/2}$ in mV)
Na_2SO_4	1:1	2.3	0
NaCl	1:1	2.2	0
Citric acid	1:1	2.5	25
Citric acid	1:1	3.2	65
Citric acid	1:1	4.4	150
Citric acid	5:1	4.1	145
Citric acid	5:1	5.0	190
Citric acid	5:1	6.0	225
NaF	2:1	3.0	54
NaF	2:1	4.0	65
$Na_4P_2O_7$	1:1	2.3	68
$Na_4P_2O_7$	1:1	4.0	170
$Na_4P_2O_7$	1:1	4.5	225
$Na_4P_2O_7$	1:1	6.0	240
Tartaric acid	5:1	2.2	3
EDTA	1:1	2.4	150
Oxalic acid	5:1	4.4	165

The stability indexes were determined as the difference between the $E_{1/2}$ of a 0.001M $Sn(ClO_4)_2$ solution and the $E_{1/2}$ of a 0.001M $Sn(ClO_4)_2$ solution containing 0.09M $KClO_4$ and the new complexer. All pH adjustments were made with carbonate free NaOH or $HClO_4$. The $Sn(ClO_4)_2$ solutions were freshly prepared by dissolving SnO in cold $HClO_4$ using a catalytic amount of mossy tin.

REFERENCES

1. Donaldson, J. D. and Moser, W. - J. Chem. Soc., 4000 (1960).
2. Sillen, L. G. and Martell, A. E. - Stability Constants of Metal-Ion Complexes, Special Publication No. 17, The Chemical Society, Burlington House, London (1964)
3. Sillen, L. G. and Martell, A. E. - Stability Constants of Metal-Ion Complexes, Special Publication No. 25, The Chemical Society, Burlington House, London (1971).