

## METHOXYSILANE PURIFICATION

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### Summary

Distillable nonionic chloride impurities at 50 to 2000 ppm Cl are conveniently removed from alkoxysilanes by treatment with sodium metal. When free of these contaminants, thought to be 2° and 3° alkyl chlorides, MeSi(OMe)<sub>3</sub> hydrolyzes substantially more slowly than before treatment.

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### Introduction

Distillable chlorine-containing impurities are commonly present at levels of 50 ppm Cl or greater in commercial alkoxysilanes. These impurities may be either chlorosilanes or alkyl chlorides, both of which generate HCl in contact with water. When reactive alkoxysilanes like MeSi(OMe)<sub>3</sub> are hydrolyzed with these impurities present, methoxy-hydrolysis and silanol condensation rates are greatly increased. Furthermore, if a product is manufactured from the hydrolyzate, its properties may be affected by traces of chloride ions or HCl formed during product use.

These two types of impurities may be distinguished by standard analytical tests. Chlorosilane impurities are detected by titrating the acid formed on dissolving the sample in isopropyl alcohol [1]. Alkyl chlorides are determined by a total chloride method, such as treatment with biphenylsodium followed by potentiometric determination of chloride [2]; the result should be corrected for any chlorosilane present. White and Olson [3] have described removing chlorosilane contaminants by distilling the methoxysilane from NaOMe. During the course of our work it was confirmed that this method reduces chloride contaminants which become acidic on treatment with isopropyl alcohol to levels below detection. However, most of the chloride contamination in commercial MeSi(OMe)<sub>3</sub> and Me<sub>2</sub>Si(OMe)<sub>2</sub> which we have tested is not hydrolyzed by isopropyl alcohol. These impurities may be alkyl chlorides formed in the Direct Process (the industrial process of treatment of silicon with MeCl to form chlorosilanes) or formed during methoxylation from the reaction of HCl with olefin byproducts of the Direct Process [5]. We were not able to significantly reduce the level of these organic chloride impurities by previously described methods [3,4]. As described in this paper, however, they are conveniently

reduced to below detectability by refluxing the methoxysilanes with metallic sodium. We have also found that  $\text{MeSi}(\text{OMe})_3$  treated in this way hydrolyzes much more slowly than the same material before treatment.

## Results and discussion

The results of our attempts to remove the covalent chloride contaminants from  $\text{MeSi}(\text{OMe})_3$  by various methods are summarized in Table 1.

Although a variety of strong bases and reducing reagents were tested, including several recommended previously [3a,4], metallic sodium dispersion was most effective. The sodium effectively reduced the level of all chloride impurities in  $\text{MeSi}(\text{OMe})_3$  obtained from three commercial sources containing various total chloride levels. We consistently obtained neutral  $\text{MeSi}(\text{OMe})_3$  with 10 ppm or less total chloride.

We presume that the sodium metal removes alkyl chlorides by a reductive process.  $\text{NaOMe}$  and  $\text{NaOH}$  are most likely also present but, they appear to be less effective in removing organic chlorides (Table 1).

Sodium dispersion is a particularly convenient reagent for this procedure. An hour of vigorous stirring with excess sodium at temperatures as low as  $75^\circ\text{C}$  followed by distillation gave neutral, nearly chloride-free methoxysilanes. Since no solvent was used, essentially all of the methoxysilane could be recovered with purities which were at least equal to those of the starting material. When methanol was present, it also reacted with the sodium, giving final methanol levels of 200 to 500 ppm (determined by FTIR). The amount of sodium required to bring chloride levels below 10 ppm obviously depends on the methanol as well as the chloride present. However, even when the methanol was first removed by azeotropic distillation, 3 to 3.5 gram atoms of sodium were required per chloride equivalent. Using lesser amounts of sodium removed only a part of the chloride.

The effect of purification on hydrolysis was also studied. The hydrolyses of various  $\text{MeSi}(\text{OMe})_3$  samples using 1/3 molar ratios of silane/water were carried out in a  $25^\circ\text{C}$  constant temperature bath with strong agitation, principally because these conditions were easily reproducible and allowed measurement of small temperature changes (i.e.  $0.1^\circ\text{C}$ ). In all cases the temperature of the reaction mixture rose

TABLE 1  
SURVEY OF REAGENTS FOR REMOVING CHLOROALKANES FROM  $\text{MeSi}(\text{OMe})_3$

Reagent	Excess (%) <sup>a</sup>	Time at reflux (h)	Total chloride concentrations (ppm)	
			Initial	Final
$\text{LiAlH}_4$	400	1	400	300
25% $\text{NaOMe}$ in $\text{MeOH}$	2200	3	400	280
Tetramethylguanidine	200	1	400	267
$\text{MgO}$	1000	5	400	360
20% $\text{KOH}$ in $\text{MeOH}$	25000	1	400	160
$(\text{C}_4\text{H}_9)_2\text{SnH}_2$	500	4	400	230
50% $\text{Na}$ dispersion	400	1	400	5

<sup>a</sup> Based on ppm total chloride measured.

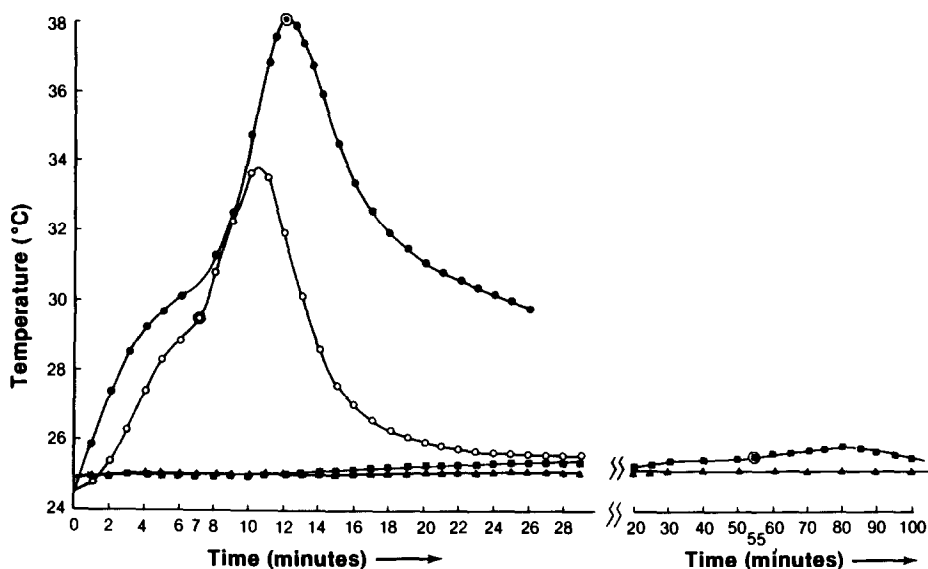


Fig. 1. Temperature profiles for  $\text{MeSi}(\text{OMe})_3$  hydrolysis reactions: ● before Na treatment, ▲ after Na treatment: ○ after treatment and spiked with *t*-butyl chloride, and ■ after Na treatment and spiked with 3-chlorohexane. The times at which the reactions became single-phased are indicated by a circle around that point; purified  $\text{MeSi}(\text{OMe})_3$  required 315 minutes.

during hydrolysis and the initially two phase reaction mixture became homogeneous at or a few minutes before the temperature maximum. Higher levels of chloride impurities gave a homogeneous reaction mixture more quickly and gave a larger temperature spike, indicating a more rapid reaction. Specifically, untreated  $\text{MeSi}(\text{OMe})_3$  containing 400 ppm covalent chloride reacted quickly, giving a  $14^\circ\text{C}$  temperature rise and forming a single phase in 12 minutes. In contrast, purified  $\text{MeSi}(\text{OMe})_3$  gave only a  $0.1\text{--}0.2^\circ\text{C}$  temperature maximum and required 5 h to become homogeneous.

Initially, we believed that the hydrolysis reactions were being catalyzed by traces of HCl or chlorosilanes, which would also be removed by the sodium. However, purified  $\text{MeSi}(\text{OMe})_3$  spiked with sufficient neutral *t*-butyl chloride to give 380 ppm organic chloride hydrolyzed at a rate very similar to that of the unpurified sample (Fig. 1). The reaction was homogeneous in 7 minutes and showed a  $9^\circ\text{C}$  temperature rise at 10 minutes. In both reactions the  $\text{MeSi}(\text{OMe})_3$ 's acid level was less than 1 ppm. A similar experiment using the secondary alkyl chloride, 3-chlorohexane, showed a much smaller catalytic effect, becoming homogeneous in 55 minutes and increasing only  $0.9^\circ\text{C}$  in temperature. Nonetheless, this was a substantially faster rate than observed for the purified  $\text{MeSi}(\text{OMe})_3$ .

This study illustrates the significance of low levels of acid producing impurities in alkoxy silanes and their potential effects on alkoxy silane reactions.

## Experimental

### Analysis

Three types of analyses were made routinely; total chloride, ionic chloride and

acidity following hydrolysis. Acidity was determined by a chlorometric titration in isopropyl alcohol, which hydrolyzes any chlorosilanes present [1]. Total chloride was determined by first treating with sodium biphenyl, which converts all chlorine present to  $\text{Cl}^-$ , followed by potentiometric titration with  $\text{AgNO}_3$  [2]. Ionic (and hydrolyzable) chloride was determined using a similar potentiometric method without the sodium biphenyl pretreatment.

It is noteworthy that 100 ppm levels of t-butyl chloride in  $\text{MeSi}(\text{OMe})_3$ , measurable as total chloride but not as ionic chloride, nonetheless gave an immediate  $\text{AgCl}$  precipitate on addition of excess aqueous  $\text{AgNO}_3$ . 3-Chlorohexane gave an  $\text{AgCl}$  precipitate after standing a few minutes. Thus, a few drops of aqueous  $\text{AgNO}_3$  will not distinguish qualitatively between tertiary alkyl chlorides and chlorosilane impurities in methoxysilanes [3a].

#### *Sodium treatment of $\text{MeSi}(\text{OMe})_3$*

$\text{MeSi}(\text{OMe})_3$  (Kay-Fries Co.) was found to contain 383 ppm organic chloride, less than 1 ppm ionic chloride and less than 1 ppm acid measured as  $\text{HCl}$ . 500 g were placed with 1.5 g sodium dispersion in paraffin (50% Na, from Alfa Chemicals) in a 1 liter, three necked Morton flask equipped with a distillation column,  $\text{N}_2$  atmosphere and an overhead stirrer. The mixture was brought to reflux with strong agitation. (Later experiments showed that 1 h at  $75^\circ\text{C}$  was adequate.) After refluxing 1 h, the  $\text{MeSi}(\text{OMe})_3$  was distilled in 2 aliquots of 400 and 78.8 g respectively giving a total yield of 95.8%. The first aliquot, when separated by GC on a 10', 10% SP-2100 column, was 99.71 area %  $\text{MeSi}(\text{OMe})_3$ , 0.035 area %  $\text{Me}_2\text{Si}(\text{OMe})_2$  and 0.25 area % unidentified high boiling material (3 peaks). The second aliquot contained 99.1 area %  $\text{MeSi}(\text{OMe})_3$ , 0.01 area %  $\text{Me}_2\text{Si}(\text{OMe})_2$  and 0.92 area % high boiling material. The aliquots contained 5 and 3 ppm organic chloride, respectively, and less than 1 ppm of both ionic chloride and acid as  $\text{HCl}$ . Two other  $\text{MeSi}(\text{OMe})_3$  samples containing 1200 and 21 ppm total chloride, were treated similarly. Their total chloride levels were reduced to 10 and 1, respectively.

#### *Sodium treatment of $\text{Me}_2\text{Si}(\text{OMe})_2$*

$\text{Me}_2\text{Si}(\text{OMe})_2$  (prepared from  $\text{Me}_2\text{SiCl}_2$ ) was found to contain 20 ppm organic chloride, 6 ppm ionic chloride and 6 ppm acid as  $\text{HCl}$ . 1500 g were placed in a 2 liter, three necked Morton flask, equipped with a distillation column, an  $\text{N}_2$  atmosphere and an overhead stirrer. 3.2 g of  $\text{Me}_2\text{Si}(\text{OMe})_2/\text{MeOH}$  azeotrope were distilled (b.p.  $60^\circ\text{C}$  [6]) and discarded. After cooling, 2 g of sodium dispersion (Alfa) were added and the mixture held at reflux with strong agitation for 2 h. 1130 g of  $\text{Me}_2\text{Si}(\text{OMe})_2$  were distilled (75% yield) and were found to be neutral and to contain less than 1 ppm of both organic and ionic chloride.

#### *$\text{MeSi}(\text{OMe})_3$ hydrolyses*

201 g of commercial  $\text{MeSi}(\text{OMe})_3$  (400 ppm organic chloride and 1 ppm of both ionic chloride and acid as  $\text{HCl}$ ) were placed in a 500 ml Morton flask with an overhead stirrer, in a  $25.0 \pm 0.1$  constant temperature bath. 79.7 g deionized water at 24 to  $25^\circ\text{C}$  were added and the stirrer turned on high (333 rpm). The temperature was measured to  $0.1^\circ\text{C}$  and the time required for the initially 2 phase system to become a single phase recorded. The reaction's temperature during hydrolysis is shown as solid circles in Fig. 1.

A similar hydrolysis was carried out using sodium treated  $\text{MeSi}(\text{OMe})_3$  which contained less than 1 ppm total chloride and less than 1 ppm acid. The temperature rise of this hydrolysis is shown as solid triangles in Fig. 1.  $\text{MeSi}(\text{OMe})_3$  spiked with t-BuCl and 3-chlorohexane were prepared by combining purified  $\text{MeSi}(\text{OMe})_3$  with sufficient alkyl chloride (first neutralized by treating with MgO) to give 400 ppm organic chloride. Analyses showed that the t-BuCl spiked sample contained 385 ppm total chloride and less than 1 ppm of both ionic chloride and HCl. The 3-chlorohexane spiked sample containing 387 ppm total chloride and less than 1 ppm of both ionic chloride and HCl. The hydrolyses were carried out as described above using the same reagent quantities. The reaction temperatures are plotted as open circles and solid squares in Fig. 1.

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