

## Silicon Determination in Low-Boiling Organosilicon Compounds by Acid Digestion

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Several methods have been proposed for the quantitative determination of silicon in organosilicon compounds\*. The best analytical method from the standpoint of accuracy is considered to be the acid digestion method<sup>1</sup>. The compound is oxidized generally by fuming sulphuric acid alone or mixed with fuming nitric acid and the residual silicon dioxide weighed. It is usual to carry out the oxidation either in a Kjeldahl flask with the mouth closed by a glass balloon or in a crucible<sup>2</sup>. The former technique is applicable to compounds with boiling points even below 100° C (*cf. Ref.*<sup>2</sup> pp. 54 and 143). The latter method is best suited to high-boiling compounds or resinous polymers, because of the losses of material which can easily take place during the initial oxidation period. This limitation to the crucible method is regrettable since from the standpoint of speed and simplicity it is superior to the Kjeldahl method. The present paper is a description of an adaption of the crucible method to the analysis of low-boiling organosilicon compounds.

The new method might be called "the double crucible method" since two transparent quartz crucibles, volumes 10 and 50 ml, respectively, are used (Fig. 1). The empty crucibles are heated over a Meker burner for 15 min and then weighed. The inner crucible is filled with a mixture of 2 ml of 60 % fuming sulphuric acid and 2 ml of fuming nitric acid ( $d = 1.50$ ) and cooled in iced water. The substance (calculated to give about 0.05 g of silicon dioxide) is weighed in a sealed glass ampoule. The tip of the ampoule is broken and the ampoule immediately placed in the acide-filled crucible as shown by Fig. 1. The substance is slowly driven out of the ampoule by heating the top with a small flame. The comparatively large depth reduces the risk of any material escap-

\* A review has been given by McHard *et al.*<sup>1</sup>

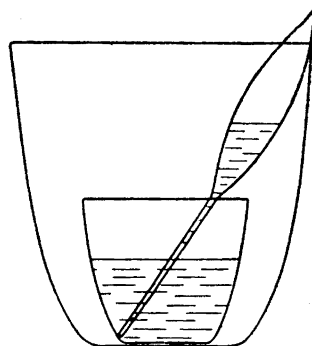


Fig. 1. Arrangement for acid digestion.

ing through the layer of acid. As soon as the ampoule is empty the heating of the crucibles is begun using a low flame. The heating must be done carefully until the sample has frothed. Most types of organosilicon compounds froth violently on digestion with a mixture of sulphuric and nitric acid, and the flame must be removed until the frothing has subsided. This tendency to froth has led to the use of the outer larger crucible which catches any overflow from the small crucible. The heating is continued until the crucibles are dry and they are heated finally over a Meker burner to constant weight. Half an hour is generally enough. Residual silicon dioxide is calculated back to silicon in the original sample.

This method is also suited to the analysis of organosilicon compounds which react violently with the acid digestion mixture *e. g.* certain aminosilanes and silazanes. Table 1 contains analytical values for trimethylethoxysilane and hexamethyldisiloxane which cannot be analysed using the ordinary crucible method (*cf. Ref.*<sup>1</sup>).

Table 1. Analysis values, using the "double crucible method".

Compound	B. p. °C (760 mm)	% Si	
		Found	Calc.
Hexamethyl- disiloxane	100	34.56	34.60
		34.41	
Trimethyl- ethoxysilane	75	23.83	23.75
		23.88	

The success of the present method depends on the following conditions which differ from those in the ordinary crucible method. The substance is weighed in an ampoule, a stronger oxidising acid mixture is used, which is cooled at the start of the reaction, a comparatively thick layer of acid hinders material from escaping, and the large outer crucible diminishes the risk of spoiling the analysis by the frothing of the mixture. As the volume of the acid mixture is kept small by the use of the inner crucible the time required for the expulsion of the acid fumes is shortened too.

1. McHard, J. A., Servais, P. C. and Clark, N. A. *Anal. Chem.* **20** (1948) 325.
2. Smith, B. *Kiselorganiska Studier* (Diss.) Gothenburg 1951.

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## A New Synthesis of Selenanthren-5,10-dioxide

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Selenanthren-5,10-dioxide (IV) is of considerable theoretical interest because it might exist in a *cis*- and a *trans*-form if there is a pyramidal configuration at the

selenium atom. Neither optical nor geometrical isomerism has been demonstrated for selenoxides in spite of several attempts<sup>1</sup>. Recently Gould and McCullough<sup>2</sup> suggested that *cis-trans* isomerism was to be expected for 1,4-di-selenane-1,4-dioxide. Owing to the great difficulties in the synthesis of 1,4-diselenane its oxidation products were never prepared. Following a suggestion of professor Arne Fredga the present author started an investigation of the oxides of selenanthren (I). Since then Gould and Burlant<sup>3</sup> have reported very promising results of a study of 1,4-diselenane. They have prepared a 1,4-dioxide and will determine its structure by X-ray methods.

The present paper describes a new synthesis of selenanthren-5,10-dioxide. A detailed report of the studies of selenanthren oxides and thianthren oxides will be published elsewhere.

Selenanthren-5,10-dioxide was first prepared by Krafft and Kaschau<sup>4</sup> by the oxidation of selenanthren with nitric acid. In 1951 Cullinane<sup>5</sup> reported a modification of the same method, and established the melting point to be 265°. He also characterized a hydrate and a dihydrochloride of IV. The present author has prepared selenanthren-5,10-dioxide in a way represented by the reaction scheme below.

The dioxide obtained by this method is identical with the product of Cullinane, as has been shown by IR-spectra (Fig. 1) and mixed melting points. The peak at 13.05  $\mu$  is due to out-of-plane vibration of the hydrogen atoms in the benzene nucleus,

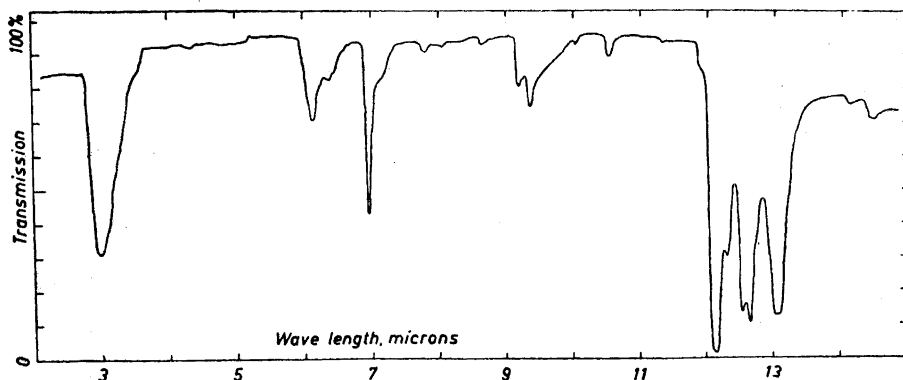


Fig. 1. Infrared absorption spectrum of selenanthren-5,10-dioxide in pressed KBr. Perkin Elmer model 21 spectrometer with NaCl prism.