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A Method of Differential Conductometric Titration of a Mixture of Methylchlorosilanes in Nonaqueous Solutions

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In recent times, monomeric and polymeric organosilicon compounds, as well as various materials based on them, have found broad practical application in various fields of science, industry, and new technology. The principal raw materials for their synthesis are alkyl-(aryl)-chlorosilanes, obtained by direct synthesis from alkyl-(aryl)-chlorides and metallic silicon ([1]).

However, until very recently, sufficiently accurate and rapid methods for the analysis of multicomponent mixtures of alkyl-(aryl)-chlorosilanes had not been developed ([2,3]). Methods for analyzing alkylchlorosilanes based on their fractional distillation and subsequent determination of chlorine in the fractions obtained ([4]), as well as the method of gas-liquid chromatography ([5]), mass spectrometry ([3]), and the combination-scattering method ([6]), require complicated apparatus for their performance, have been little developed, and therefore have not yet been introduced into practice. Other methods also exist for the analysis of alkyl-(aryl)-chlorosilanes ([7–9]), but they are applicable to the determination only of individual compounds.

We have developed a new method for the differential quantitative determination of individual methylchlorosilanes in binary and three-component mixtures consisting of trimethylchlorosilane, dimethyldichlorosilane, and methyltrichlorosilane. The method is based on the preliminary quantitative conversion of alkylchlorosilanes into alkylthiocyanate-substituted derivatives by means of ammonium thiocyanate and subsequent conductometric titration of the alkylthiocyanatosilanes with a benzene solution of dimethylaminoantipyrine in an acetonitrile–ether medium.

Experimental Part

The objects of our investigation were trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, and their binary and three-component mixtures. The initial methylchlorosilanes were purified and had physicochemical constants corresponding to the literature data. Solutions of methylchlorosilanes were prepared in dry benzene. For titration we used a 0.1 M benzene solution of dimethy-

Fig. 1 and Fig. 2: conductometric titration curves

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laminoantipyrine, prepared from an accurately weighed portion of the reagent. Dimethylaminoantipyrine was used by us as a titrant for the first time. Dimethylaminoantipyrine was recrystallized from water and kept in a thermostat at a temperature of 105° to constant weight. Ammonium thiocyanate was prepared as a 0.3 M solution in acetonitrile. The titration was carried out in a closed-type cell with platinized platinum electrodes in the form of plates (1 × 1 cm), sealed into the cell cover. The setup for conductometric titration was assembled from

of the following parts: an R-38 rheostat resistance bridge, a ZG-1 audio-frequency generator, and an INO-3M null-indicator instrument.

Procedure for determination. Into the cell for conductometric titration is poured a mixture of solvents consisting of 2 parts (by volume) acetonitrile and 3 parts diethyl ether. The solvent mixture has sufficient electrical conductivity for the present titration and ensures precipitation of the products of the chemical reactions taking place. To the prepared solvent mixture, benzene solutions of methylchlorosilanes are added from a micropipette, and titration with ammonium thiocyanate is begun.

Fig. 1. Curves of conductometric titration of binary mixtures of methylthiocyanato-substituted silanes with 0.1 M benzene solution of dimethylaminoantipyrine in an acetone–diethyl ether medium:
1 —methyltrithiocyanatosilane + dimethyldithiocyanatosilane;
2 —trimethylthiocyanatosilane + dimethyldithiocyanatosilane;
3 —trimethylthiocyanatosilane + methyltrithiocyanatosilane;
4 —curve for replacement of chlorine atoms in alkylchlorosilanes by thiocyanate groups.

Fig. 2. Curves of conductometric titration of three-component mixtures of methylthiocyanato-substituted silanes with 0.1 M benzene solution of dimethylaminoantipyrine in a diethyl ether medium:
1 —trimethylthiocyanatosilane + dimethyldithiocyanatosilane + methyltrithiocyanatosilane (in the ratio 1 : 1 : 1);
2 —trimethylthiocyanatosilane + dimethyldithiocyanatosilane + methyltrithiocyanatosilane (in the ratio 1 : 2 : 2).

In this process an exchange reaction occurs—the interaction of methylchlorosilanes with ammonium thiocyanate according to the equation

$$(\mathrm{CH_3})_n\mathrm{SiCl}_{4-n} + (4-n)\mathrm{NH_4SCN} \rightarrow (\mathrm{CH_3})_n\mathrm{Si(SCN)}_{4-n} + (4-n)\mathrm{NH_4Cl}.$$

Ammonium thiocyanate is added from a burette until a sharp decrease in the resistance of the solution being analyzed occurs, accompanied by cessation of precipitation of ammonium chloride. Since an excess of ammonium thiocyanate is harmful in carrying out subsequent operations, it is recommended first to determine, by means of a blank experiment, the volume of ammonium thiocyanate required for replacement of the chlorine atoms. After titration of the methylchlorosilane mixture with ammonium thiocyanate, the resulting substitution products are titrated with 0.1 M benzene solution of dimethylaminoantipyrine. The resistance of the solution being analyzed is measured after each successive addition of 0.02–0.04 ml of reagent.

The nature of the conductometric titration curves for mixtures of methylthiocyanato-substituted silanes is shown in Figs. 1 and 2. Figure 1 gives titration curves for various binary mixtures of methylthiocyanato-substituted silanes. Figure 2 presents conductometric titration curves for three-component mixtures of methylthiocyanato-substituted silanes.

Analysis of the conductometric titration curves shows that first to be titrated is the thiocyanate derivative obtained from methylchlorosilane containing the smallest number of chlorine atoms. Then dimethyldithiocyanatosilane is titrated and, finally, methyltrithiocyanatosilane—the derivative of methyltrichlorosilane, which contains the largest number of chlorine atoms in the molecule among the possible methylchlorosilanes.

Experimentally, the smallest amounts of methylchlorosilanes that can be determined in a mixture by the proposed method have been established: $(CH_3)_3SiCl$, not less than 0.0055 g; $(CH_3)_2SiCl_2$, not less than 0.0025 g; and CH_3SiCl_3, not less than 0.0023 g in 12 ml of mixed solvent. In the case of very high concentrations of methylchlorosilanes, the solution being analyzed should be diluted.

The results of quantitative analysis of binary mixtures of methylchlorosilanes are presented in Table 1.

Table 1

Results of quantitative analysis of binary mixtures of methylchlorosilanes by the conductometric titration method

Composition of the mixture analyzed	Taken, g	Found, g	Error, %
A 1) $(CH_3)_3SiCl$	0.00423	0.00423	0
A 1) $(CH_3)_2SiCl_2$	0.00320	0.00314	−2.0
A 2) $(CH_3)_3SiCl$	0.00538	0.00541	+0.6
A 2) $(CH_3)_2SiCl_2$	0.00412	0.00407	−1.3
B 1) $(CH_3)_2SiCl_2$	0.00320	0.00315	−1.7
B 1) CH_3SiCl_3	0.00228	0.00231	+0.9
B 2) $(CH_3)_2SiCl_2$	0.00412	0.00420	+2.0
B 2) CH_3SiCl_3	0.00342	0.00346	+1.2
C 1) $(CH_3)_3SiCl$	0.00423	0.00428	+1.2
C 1) CH_3SiCl_3	0.00228	0.00232	+1.8
C 2) $(CH_3)_3SiCl$	0.00538	0.00538	0

Composition of the mixture analyzed	Taken, g	Found, g	Error, %
C 2) CH_3SiCl_3	0.00342	0.00346	+1.2

The data in Table 1 show that the analysis of two-component mixtures of methylchlorosilanes can be carried out by the conductometric titration method with sufficient accuracy. The relative error of the determinations is ±2%.

The results of quantitative analysis of three-component mixtures of methylchlorosilanes are presented in Table 2.

Table 2

Results of quantitative analysis of three-component mixtures of methylchlorosilanes by the conductometric titration method

Composition of the mixture analyzed	Taken, g	Found, g	Error, %	Composition of the mixture analyzed	Taken, g	Found, g	Error, %
1) $(CH_3)_3SiCl$	0.00423	0.00423	0	2) $(CH_3)_3SiCl$	0.00211	0.00212	+0.6
1) $(CH_3)_2SiCl_2$	0.00320	0.00316	−1.4	2) $(CH_3)_2SiCl_2$	0.00320	0.00324	+1.3
1) CH_3SiCl_3	0.00228	0.00231	+2.0	2) CH_3SiCl_3	0.00228	0.00224	−1.9

The data in Table 2 show that, in the case of three-component systems, the quantitative analysis of each component included in the mixture can be carried out with sufficient accuracy if the concentrations of methylchlorosilanes are not below the limiting values. The relative error of determinations of individual methylchlorosilanes in a three-component mixture by the proposed method is ±2%.

Thus, the proposed method for the quantitative determination of alkylchlorosilanes is distinguished by rapid execution and accuracy and can be successfully applied to the analysis of individual alkylethoxychlorosilanes and their multicomponent mixtures, methods for the differentiated determination of which have not been described in the literature.

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Note: Figure translations are in progress. See original paper for figures.