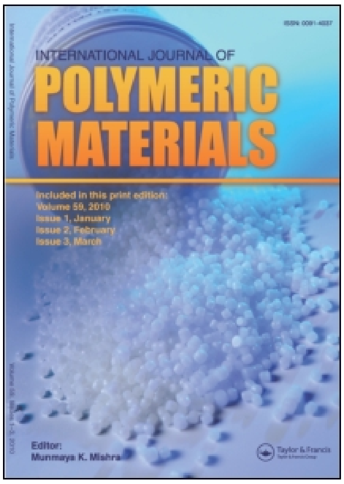

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Size-exclusion Chromatography of Highly Active Organometallic and Multifunctional Metal-containing compounds

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Some results of size exclusion chromatography (SEC) investigations of highly active organometallic and metal containing highly active compounds (OMC) are reviewed. Until recently these classes of compounds have not investigated by chromatography. New labile multifunctional metal-containing oligomers is revealed. The further applications of SEC investigation for MW-analysis of high-active OMC and multifunctional elementoxide compounds are outlined.

Keywords: Size exclusion chromatography; highly active compounds; aluminium-trialkyls; hydrolysis; organometallics

Some highly active organometallic compounds (OMC) are unstable. These monomers and oligomers undergo quick changes and are readily hydrolyzed and oxidized. Until new, the adsorption liquid chromatography [1] (LC) has not been applied to highly active OMC, because these compounds react irreversibly with inorganic sorbents. It seems perspective to study the possibilities of size exclusion chromatography (SEC) to determine molecular weight (MW) distributions of active OMC and multifunctional metal-containing compounds. If correct evaluations of SEC data on OMC were possible, even their characterization would be essential.

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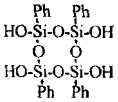
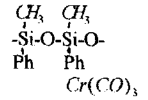
PECULIARITIES OF THE METHOD

The methods used are typical for handling spontaneously combustible OMC. All operations were carried out in inert atmosphere. The eluents were carefully dehydrated and kept in darkness and inert atmosphere with solid metal hydrides. Before the analysis the chromatographic (C) columns were calibrated for example, by the solutions of $[Me_3Si]_2NH$ for multifunctional organosilane compounds (OSC), $Al(iC_4H_9)_3$ for organoaluminium compounds (OAC), – $TiCl_4$ for titanium chlorides.

To analyze the compounds with highly reactive properties the calibration of the C column was carried out using the substances been analyzed until the accurate reproduction of the results is provided. The standards for these investigations are not available. These standards were synthesized (for example, by hydrolytic condensation of $Si(OC_2, H_5)_4$), or selected experimentally from oligomers or monomers of the class of substances investigated, preparatively separated, and characterized using independent methods. The data on some substances used for calibration are presented in Table I (column 100/0.9 cm, gel SDV-J,

TABLE I Experimental data and Moore's equation for elementoxide oligomers

Initial monomer or oligomer link	*Experimental MW*	*Experimental lg M*	*Experimental V_e, ml*	*Moore's equation V_e=*
 $\begin{matrix} Ph & Ph \\ HO\text{-}Si\text{-}O\text{-}Si\text{-}OH \\ O & O \\ HO\text{-}Si\text{-}O\text{-}Si\text{-}OH \\ Ph & Ph \end{matrix}$	1122	3.05	30	173.4–47.0 lg M
	1740	3.24	20	
 $\begin{matrix} CH_3 & CH_3 \\ \text{-}Si\text{-}O\text{-}Si\text{-}O\text{-} \\ Ph & Ph \\ & Cr(CO)_3 \end{matrix}$	720	2.857	39.5	
	1360	3.133	26.5	175.5–47.6 lg M
	1470	3.167	24.5	
	1660	3.220	23.0	
	190	2.279	58.0	
$TiCl_4$	249	2.397	53.0	139.99–35.99 lg M
	317	2.501	50.0	
	340	2.532	41.7	
$Ti(OC_4H_9)_4$	550	2.740	35.6	101.25–23.8 lg M
	760	2.881	31.0	
	1630	3.2124	24.5	
$Al(C_2H_5)_3$	117_{th}	2.057	34.0	53.52–9.52 lg M
	186_{th}	2.268	32.0	
$Al(iC_4H_9)$	198	2.299	28.0	50.94–9.84 lg M
	298	2.475	26.0	

granules 0.2–0.5 mm, eluent–dried toluene, 2 ml/min, refractometer RIDK-101 CSFR). The ratios given in examined range of molecular weights (MW) the beginning of sizing scale – in semilogarithm coordinates 1 g MW (or M) – V_e is closed to linear (Fig. 1) [2].

RESULTS AND DISCUSSION

Aluminiumtrialkyls (AA) and their derivatives aluminiumalkylhaiogenides and other OAC are separated on the SEC columns by the sieve mechanism. SEC of the samples of industrial AA show (Fig. 2) the presence of some OAC with a different MW.

The example of molecular weight state alteration in aluminiumtriethyl homogeneous hydrolysis process at the room temperature is shown (Fig. 3).

To increase the separation efficiency of magnesium-AA super crosslinked gel stirosorb was used [3]. In toluene solutions of compounds investigated transformations of the type

$$Mg_nAl_mR_{2n+3m} = MgR_2 + AlR_3$$

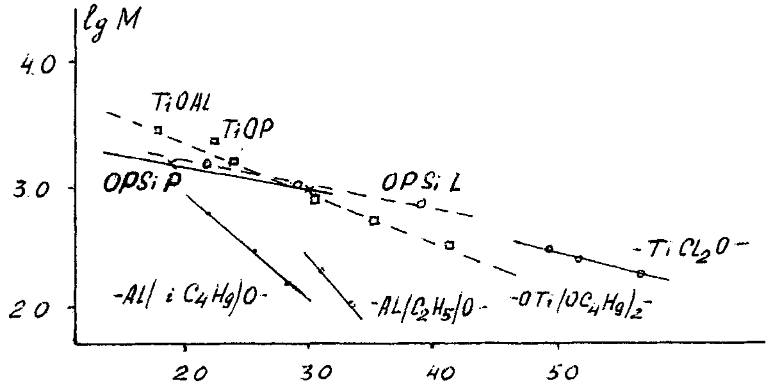


FIGURE 1 Calibration curves to different high-active organoelement compounds. Column 100/0.9 sm., SDV-J, toluene, 2 ml./min. OPSiL – organopolysiloxane linear, OPSiP – organopolysildxane polycyclical; TiOAl, TiOP – the specimens of unimodal oligomers with groups shown.

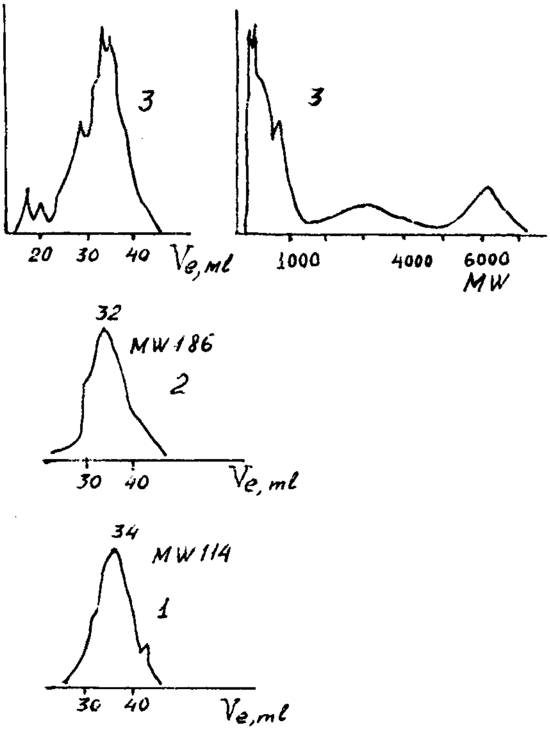


FIGURE 2 Chromatograms and molecular weight distribution (MWD) curve for the samples industrial alumuniumethyles: 1 – alumuniumtriethyl, 2 – tetraethyldialumoxane, 3 – products of aluminiumtriethyl hydrolysis. Column 100/0.9 cm, SDV-J, toluene, 2 ml/min.

and other association–dissociation reactions take (Fig. 4). SEC of Mg-AA shows, that their nature is more complex, than it might have been expected on the basis of data of cryoscopy and other methods of investigation.

Grignard's reagent (Gr) leave the column forming a peak (with positive Gilman test) with in upper part is tripled, forming a treetop crown (Fig. 5). The treatment of Gr by dioxane-1,4 results in its symmetrization [4]:

$$2C_4H_9MgCl{*}2O(C_2H_5)_2 \xrightarrow{\text{dioxane}-1,4} (C_4H_9)_2Mg{*}\text{dioxane-}1,4$$
$$+ MgCl_2{*}O(C_2H_5)_2 \rightarrow [MgCl_2]_x.$$

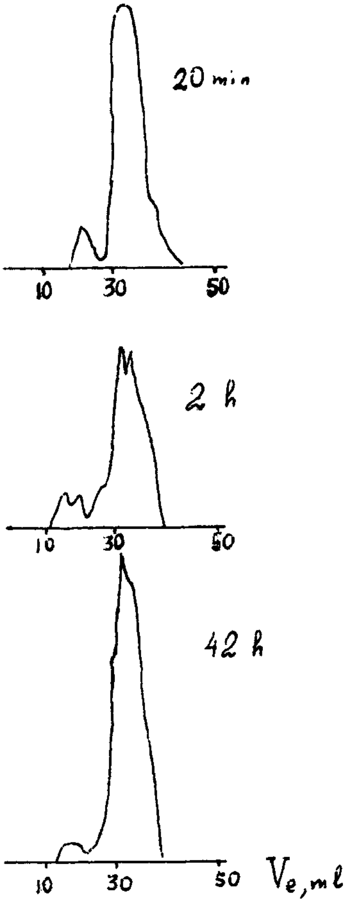


FIGURE 3 Chromatograms for triethylaluminium homogenous hydrolysis products in toluene. Original mol relationship $Al(C_2H_5)_3 : H_2O$ = 1:0.857. Column 100/0.9 cm., SDV-J, toluene, 2 ml/min.

The SEC data are in conformity with generally accepted opinion [4]. The descriptions of the direct methods of determination of high-molecular components in technical $TiCl_4$ are not available. The use of SEC allows their preliminary estimation to be made. In the cubic residue after a single distillation of technical $TiCl_4$ (Fig. 6) there are both high- and low-molecular substances (Tab. II). The possibility of preparative insolation of the oligomer components is then precondition for the calibration correction of the further elucidation MW [5]. The

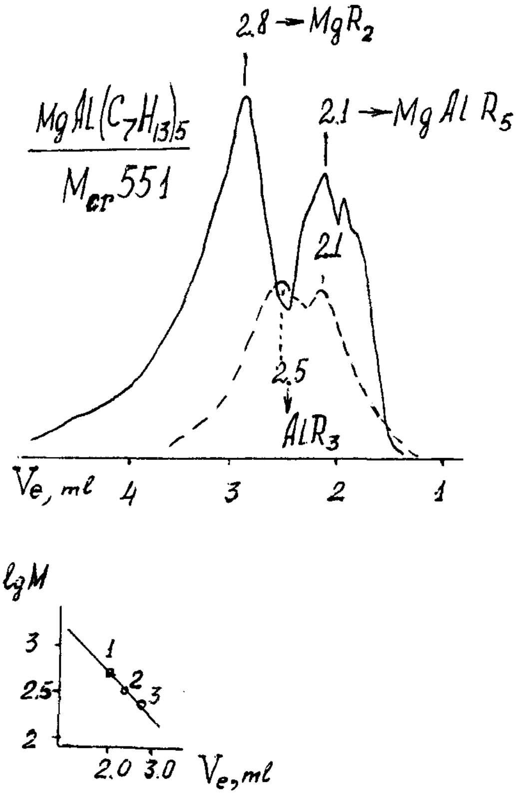


FIGURE 4 Chromatograms and calibration curve with standards used for magnesium-aluminiumalkyls. Gel-stirosorb, column 260/4 mm, toluene, 2ml./min. 1-MgAl$(C_7H_{15})_5$, M_{th} 546. 3. 2- Al$(C_7H_{15})_3$, M_{th} 324. 3-Al$(C_5H_{11})_3$, M_{th} 240.

differental curve of the distribution MW for homogenous hydrolysate of Ti$(OC_4H_9)_4$ shows the presence of a substance (Fig. 7), equal to Ti$(OH)_4$ by its MW.

Germaniumalkylchlorides leave the column by correspondence to decrease their molecular weights. V_e-lg M relationship (350 – 120 Dalton) is linear (Fig. 8). The etherates $HGeCl_3^*O(C_2H_5)_2$, $GeCl_2(GeBr_2)^*O_2$ $(C_2H_4)_2$ are introduced to column, but unsolvative $HGeCl_3$, $GeCl_2$ $(GeBr_2)$ leave the same column.

The interaction of $SnCl_4$ with excess Ti$(OC_4H_9)_4$ gives resinous noncrystallizing product. This product readily decomposes upon distillation; its main fraction according to SEC-data has 1260 Dalton

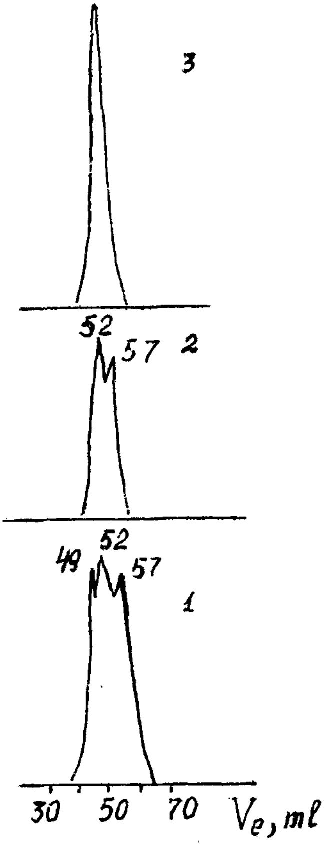


FIGURE 5 The products of $C_2H_9MgCl^*2(C_2H_5)_2O$ transformations by dioxane-1,4: 1 – initial, 2 – a loss of dioxane, 3 – an excess of dioxane. Column 750/8 mm., SDV-J, toluene, 3ml./min.

(Fig. 9). During this interaction C_4H_9Cl is distilled off near to equimolecular quantities. The liquid product has catalytic activity during liquidphase oxidation of $nC_{15}H_{32}$ by oxygen to acid, equal to that of Co stearate. MW for $Sn[OTi(OC_4H_9)_3]_4$ is 1250 Dalton [6].

Individual $Ti(OC_2H_5)_4$. $SnCl_4$ or their mixtures have not any catalytic properties. It may be assumed that the origin of the catalytic activity observed results from formation of the Sn–O–Ti fragment. Other alkoxides of two oxygenbonded elements (for example Al–O–Si,

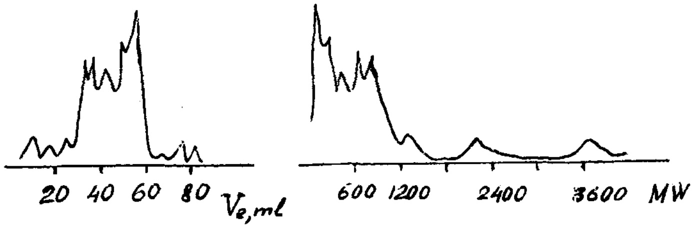


FIGURE 6 Chromatogram and differential MWD curve for the sample of cubic residue after a single distillation of technical Ticl$_4$. Column 100/1 cm., toluene, 2ml./min, SDV-J.

TABLE II Compound, present in cubic residue after a single distillation and in the partial hydrolyzed sample $TiCl_4$

V_e, ml	M_{soc}	M_{theor}	Probable formula
64.5	126	116	$Ti(OH)_4$
58	190	190	$TiCl_4$
50	317	325	$(Cl_3Ti)_2O$
44	464	460	$Cl_3Ti(OTiCl_2)_2Cl$
37.5	706	730	$Cl_3Ti(OTiCl_2)_4Cl$
35	830	865	$Cl_3Ti(OTiCl_2)_5Cl$
28	1299	1270	$Cl_3Ti(OTiCl_2)_8Cl$
20	2162	2215	$Cl_3Ti(OTiCl_2)_{15}Cl$
12	3620	3565	$Cl_3Ti(OTiCl_2)_{25}Cl$

Al–O–Ti, Ti–O–P, *etc.*) have been obtained analogically and estimated in terms of MW distribution. The condensation products for interaction $AlBr_3$ with $Si(OC_2H_5)_4$ excess SEC characteristic curve is shown (Fig. 10). The use of SEC allows one to control the interaction of components and to stop it at a necessary moment.

Ti- and Al- contain high-molecular substances are formed upon homogenous interaction of $(acac)_2TiCl_2$ and $(C_2H_5)_2AlCl$ (Fig. 11). These high-molecular catalysts are responsible for formation of polypropen. These catalysts may be characterized by the growth of their MW followed by the loss of their solubility with next precipitation and loss of catalytic properties. The deposition of these homogenous catalysts (nuclei or clusters) on the surface of polymer gel substrates [7] excludes polycondensation, that leads to the decay of active catalytic centers. The stability of catalytic systems deposited on

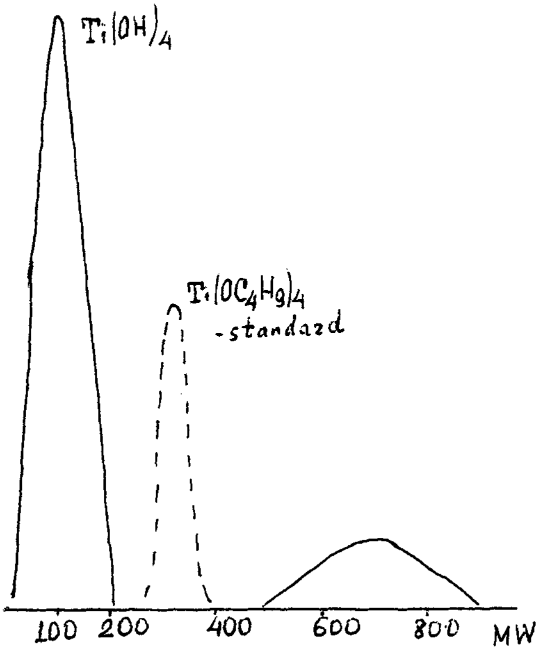


FIGURE 7 The MWD curve of tetrabutyltitanate homogenous hydrolysis products. Column 100/1 cm., toluene, 2ml./min, SDV-J.

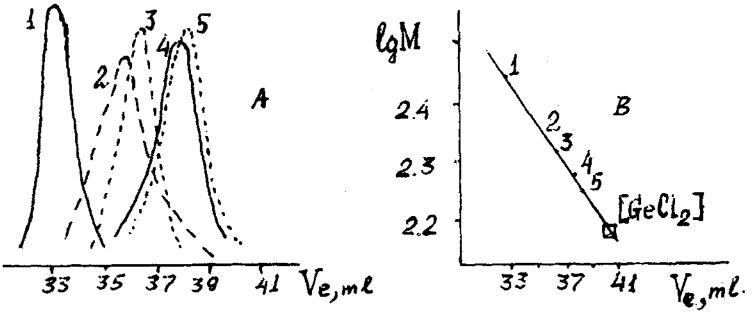


FIGURE 8 A – SEC monomer alkylgermaniumchlorides and chlorgermaniums: 1 – $(C_4H_9)_3GeCl$, 2 – $GeCl_4$, 3 – $(C_2H_5)_2GeCl_2$, 4 – $HGeCl_3$, 5 – $(CH_3)_2GeCl_2$; B – lgM-V_e relationship for germaniumchlorides. Column 80/0.8 cm., SDV-J, toluene, 2ml./min.

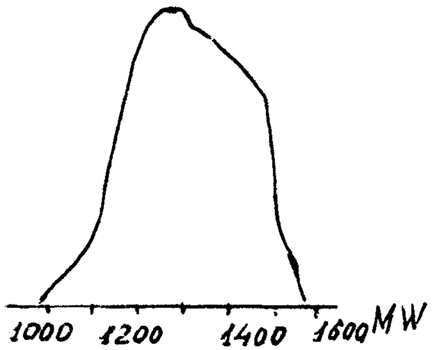


FIGURE 9 The MWD curve of interaction $SnCl_4$ with $Ti(OC_4H_9)_4$ excess products. Column 100/0.9 cm., SDV-J, toluene, 2ml./min.

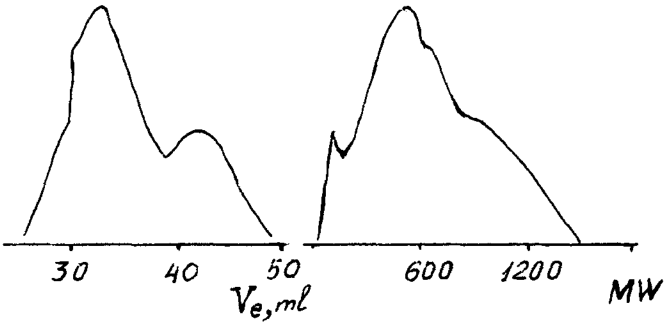


FIGURE 10 Chromatogram and MWD curve for interaction $AlBr_3$ with $Si(OC_2H_5)_4$ excess products. Column 100/0.9 cm., SDV-J, toluene, 2ml./min.

polymer gels as well as the stability of their action [7] at temperatues to 200°C increase.

SEC-investigations for products of hydrolysis $Si(OC_2H_5)_4$ allow one to define more precisely the concepts notions about chemical nature of this process (Fig. 12) to establish the destruction instability of siloxane oligomers (acid catalysis) under normal conditions [8].

The indicated examples don't restrict the scopes for investigation high-active elementcontaining oligomer compounds.

These initial results (MWD for alumoxanes, titaniumoxanes, siloxanes, *etc.*) may be practically useful [9–12].

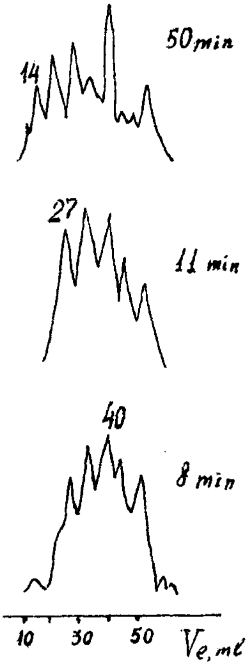


FIGURE 11 Chromatograms for dissolved Ziegler catalytic complex $Al(C_2H_5)_2Cl$–$(acac)_2TiCl_2$; column 90/1 cm, SDV-J, toluene, 2 ml./min.

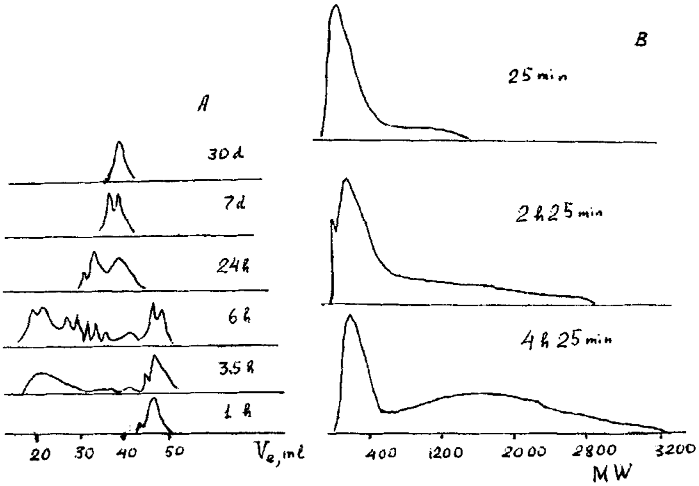


FIGURE 12 Chromatograms and MWD curves for tetraethoxysilane homogenous (acid HCl – A and base NH_3^* H_2O – B) hydrolysis products. Original mol relationships $Si(OC_2H_5)_4$:H_2O A – 2.75:1; B – 2.1:1. Hydrolysis products behavior during different time is shown. Column 100/0.9 cm., SDV-J, toluene, 2 ml./min. Data to gel sephadex LH-20 in toluene, dioxane-1,4,tetrahydrofurane are analogical.

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