A detailed study of retention of the variety of volatile organic solvents (VOS) and organophosphorus compounds on the polydimethylsiloxane (PDMS) preliminary characterized by FTIR and DSC methods was carried out by means of an inverse gas chromatography technique. The specific retention volumes and infinite dilution activity coefficients were determined for different classes of VOCs, linear and cyclic alkanes, chloroalkanes, oxygen compounds (alcohols, ketones, and esters), and nitriles as well as for typical organophosphorus compounds, 4-nitrophenyl esters of diethyl phosphoric (paraoxon) and diethyl thiophosphoric (parathion) acids. The effect of dipole-dipole interactions and dispersion interactions on the efficacy of the retention of the studied compounds on the PDMS was analyzed. Organophosphorus stimulants are characterized by strong retention on the PDMS, the difference in their retention are to be connected with more efficient dipole-dipole interaction of the oxygen atom of paraoxon with the PDMS than that of the sulphur atom of parathion. A possibility of using PDMS as a base for the detection layers sensitive to organophosphorus compounds was demonstrat