

ABSTRACT

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New capabilities of the method of negative-ion mass spectrometry with resonant electron capture for structural-analytical studies of organic compounds

Through a comprehensive consideration of theoretical principles and an analysis of the obtained experimental data on the fragmentation of negative molecular ions formed by resonant capture of low-energy electrons, the aim of the study was achieved, consisting in the development of new methods for the identification of substances on a modern production quadrupole gas chromatographic mass-spectrometric complex and in a systematic, comprehensive assessment of the effectiveness of using the MS NI REC method for the analysis of low-molecular-weight compounds of various classes. It has been shown that the use of the MS NI REC method is advisable, in particular, to identify electrophilic compounds, as well as to mutually complement the data of the MS EI PI method, since the complementary use of data from the two methods significantly increases the reliability of identification. In comparison with existing techniques, the developed methods of applying the MS NI REC method and the identification algorithms made it possible to reduce the number of analytical instruments used, significantly reduce the financial costs for their purchase and maintenance, and the consumables used. The databases created in the course of the work, of experimentally obtained and calculated mass spectra of negative ions of the studied compounds, have high concordance metrics, make it possible to significantly reduce the time spent on the process of identifying the studied compounds, and increase the likelihood of the correct result.

In the course of the work, the following results were obtained:

1. A method has been developed for recording two-dimensional mass spectra of negative ions of resonant electron capture on a quadrupole chromatograph-mass spectrometer, covering all resonance regions of the substances under study, making it possible to perform high-throughput (routine) analysis by the MS NI REC method across broad series of organic compounds.
2. The processes of fragmentation of molecular negative ions obtained by on the resonance capture of low-energy electrons, previously unstudied on a quadrupole mass spectrometer by the MS NI REC method, for classes of organic compounds: dithiodiglycols, phosphates, phosphonates, pyrophosphates, chlorophenols, nitrotoluenes, and individual compounds of other classes (more than 100 substances).
3. Methods have been developed: for the identification of V-agents, allowing the structures of the O-alkyl and P-alkyl radicals of these compounds to be established; for determining the number of carbon atoms in each O-alkyl chain in the molecules of polyesters of phosphoric acids: $(XP(O)(OR)(OR'))$, $P(O)(OR)(OR')(OR'')$, where $X = Cl$ or an alkyl radical; R, R', R'' are alkyl radicals; as well as in the molecules of tetraalkylpyrophosphates.
4. An algorithm has been developed for predicting MS NI of phosphorus-containing compounds: homologs of O-alkylalkylfluorophosphonates, V-agents, as well as chlorophosphates. When comparing experimental NI mass spectra with calculated mass spectra using the Identity and Similarity comparison algorithms, the forward and reverse search scores are in the range from 750 to 990 units. It has been shown that the results of quantum-chemical calculations of the thermochemical parameters of molecules and the energies of dissociative reactions under resonance electron capture are consistent with the experimental data.
5. The practical advantages of applying the MS NI REC method have been demonstrated, which consist of:
 - obtaining additional analytical information about the structure of compounds, including the presence of functional groups, halogen atoms, as well as their positions in the structure of the compound;
 - the ability to distinguish isomers of organic compounds;
 - the registration and establishment of the peak of molecular (deprotonated molecular) ions of various

classes of organic compounds and individual substances, for example: O-alkylalkylfluorophosphonates, O-alkyl-S-2-(N,N-dialkylamino)ethyl alkyl thiophosphonates, chloroacetophenone, dibenzoxazepine, and others;

– in the increased sensitivity to electrophilic compounds, compared with "classical" electron ionization mass spectrometry with detection of positive ions.

6. It has been experimentally confirmed that NI MS exhibits good concordance and inter-instrument reproducibility, which makes it possible to use the mass spectral databases "Varh bz" and "Progn oz" created in this work for the identification of organic compounds. The identification limit for TNT by the MS NI REC method was established to be 5 ng.

7. The advisability of including the MS NI REC method in widespread practice for solving analytical problems is due to a combination of the following factors: good inter-experimental concordance and inter-instrument reproducibility, the advantages of practical application demonstrated in this work, and the simplicity of the instrumentation.