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Determination of Impurities in High-Purity Methyl Methacrylate by Chromadistillation Coupled with Atmospheric Pressure Photochemical Ionization Mass Spectrometry

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Abstract—The determination of impurities in high-purity substances is an urgent task. A combination of chromadistillation with atmospheric pressure photoionization mass spectrometry can help in its solution. A combination of these methods ensures recording mass spectra of impurities contained in high-purity organic substances without separating them from the main component. At that, ions of the main component, formed as a result of atmospheric-pressure photoionization, act as a reagent substance for the desired impurities in the atmospheric pressure photochemical ionization mode. It is possible to choose conditions under which the number of peaks recorded in the mass spectrum of a mixture corresponds to the number of mixture components, and each peak corresponds to M^+ or MH^+ ions of the mixture component. The information obtained is the number of impurities in the test substance (in this work, in methyl methacrylate) and their integer molecular weights.

Keywords: chromadistillation, atmospheric pressure photo- and photochemical ionization mass spectrometry, high-purity organic substances, methyl methacrylate, impurities

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The determination of low-molecular-weight volatile and medium volatile impurities in high-purity organic substances when the concentration of the main component is much higher than the concentration of impurities present in the mixture and the number of these impurities and their nature are unknown is a difficult task. In using gas chromatography–electron ionization mass spectrometry (GC–EI MS) to solve such a problem, during the release of the main component from the column it is desirable to redirect the carrier gas flow to another detector (e.g., flame ionization) or to a discharge (e.g., using Dean’s flow switching system) [1]. Another variant is to turn off the ion source cathode during the elution of the main component. In both cases, information about impurities eluting from the column along with the main component is lost. When composition of impurities is unknown, the problem cannot be solved by GC–MS.

New opportunities for detecting analytical signals of impurities in high-purity volatile organic substances against the background signal of the main component are opened up using chromadistillation coupled with atmospheric pressure photoionization mass spectrometry [2]. In this method, when the vapor zone of the main component and the impurities passes through the ionization chamber, they are softly ionized by UV radiation and the impurities are photo-

chemically ionized by the formed ions of the main component [3]. In this case, vapors of the main component act as a reagent substance. The number of peaks recorded in the mass spectrum of the mixture may correspond to the number of components of the mixture, and each peak may correspond to M^+ ions or MH^+ ions of the mixture component. The number of peaks recorded in the mass spectrum can exceed the number of impurities due to registering cluster ions of the main component and impurities $(M^+)n$, $(M^+M_{imp})m$, or $(MH^+M_{imp})n$. These peaks are an additional proof of the registration of M^+ and MH^+ ions and, accordingly, the molecular masses of impurities. Cluster ions can be taken into account and excluded from the mass spectrum by increasing the temperature of the ion source. The obtained data also provide information on the number of impurities co-eluting with the main component, which expands the number of detectable components of the analyzed mixture of unknown composition. The sensitivity of impurity determination in this case can be two orders of magnitude higher than that of photoionization mass spectrometry (APPIMS) [4].

Unlike chromatography, separation in chromadistillation occurs in an empty quartz capillary with a temperature gradient along its length in a carrier gas

flow as a result of repeated acts of evaporation and condensation. Chromadistillation provides the formation of a step (zone) of a constant concentration of vapors of the main component in the gas flow in terms of concentration for a certain time, determined by the volume of the analyzed sample [5], the temperature of the final section of the capillary, and vapor pressure of the main component at this temperature.

According to the theory of chromadistillation, the frontal portion of such a step should be enriched with more volatile impurities than the main component, and the final portion should be enriched with higher-boiling impurities [6]. Thus, the group separation of impurities without their complete separation from the main component is attained.

In the case of a combination of chromadistillation with APPIMS, impurities are recorded during their photochemical ionization in the ion source without their preliminary separation from the main component.

The aim of this work was to record the number of impurities in a sample of methyl methacrylate (MMA) (with obtaining information about the estimated integer molecular weight) using chromadistillation coupled with atmospheric pressure photochemical ionization mass spectrometry (CD/APPCIMS).

EXPERIMENTAL

In this work, a Finnigan model 4021 chromatography–mass spectrometer (United States), with an atmospheric pressure photoionization (APPI) ion source developed by us [7] was used.

A krypton gas-discharge lamp with photon energy of 10.6 eV was used as a source of UV radiation. The temperature of the chromatograph injector and the temperature of the ion source were 250°C. The volume of the analyzed sample of methyl methacrylate (density—0.94 g/mL, boiling point—101°C) was 1 μ L. To provide the chromadistillation mode, the MMA

sample was introduced into the injector of the gas chromatograph at 250°C using a microsyringe. The MMA vapors in a helium flow entered a quartz capillary with an inner diameter of 0.25 mm and a length of 2 m cooled to room temperature. Then, the vapors of condensed MMA in a carrier gas flow entered the ionization chamber of the ion source through a line heated to 250°C. At the end of the recorded step, ballistic heating of the capillary to a temperature of 250°C was carried out for the rapid evaporation of high-boiling impurities. The ions formed as a result of atmospheric pressure photoionization and photochemical ionization (reagent substance—vapors of the main component) entered the high-vacuum region of the mass analyzer (quadrupole). Registration was carried out in the total ion current mode. Mass spectra were scanned in the m/z range of 40–500 amu.

RESULTS AND DISCUSSION

The mass spectra recorded during the exit of the MMA chromadistillation stage exhibited a number of peaks with characteristic m/z values (peaks with intensities higher than 2 rel % were considered), presumably corresponding to impurity substances with molecular weights in the range from 68 to 242 amu (Table 1). This conclusion was made on the basis of studies of APPCI mass spectra of various known compounds, which we performed earlier at an ion source temperature of 250°C. These studies have shown that the mass spectra of many organic compounds consisted of a single peak of the M^+ ion and, more rarely, of two peaks of M^+ and MH^+ ions. These data allowed us to make assumptions about the values of molecular weights of the detected impurities. According to *GOST 20370-74* [8], MMA is characterized by eight impurities with molecular weights of 32, 58, 74, 86, 102, 110, 114, and 116, the total concentration of which is less than 0.15%. Five of them are given in Table 1. In addition to these substances, 29 more components were identified as a result of this study.

Table 1. Estimated molecular weights* of impurities in a methyl methacrylate sample recorded by chromadistillation coupled with atmospheric pressure photochemical ionization mass spectrometry

No.	Molecular weight	No.	Molecular weight	No.	Molecular weight	No.	Molecular weight
1	68	10	110	19	120	28	178
2	72	11	112	20	144	29	180
3	78	12	114	21	146	30	186
4	84	13	116	22	154	31	196
5	86	14	118	23	156	32	218
6	96	15	120	24	158	33	220
7	100 (MMA)	16	126	25	162	34	242
8	102	17	128	26	168		
9	104	18	140	27	176		

* Molecular weights were calculated on the assumption that the registered m/z values in the mass spectra correspond to M^+ or M^+ and MH^+ .

A combination of the proposed approach with high-resolution mass spectrometry would ensure the identification of impurities with a high probability. The mass spectra of these impurities were recorded in this study. Information about the estimated integer molecular weights of impurities is also of practical importance for experts involved in the synthesis, isolation, and purification of thermostable organic substances and the synthesis of other substances from them. This information is important both in case of coincidence (or difference by 1 amu) with the molecular weights of the substances used in the synthesis or possible reaction by-products, and in the case of the determination of additional unknown compounds. The proposed approach is a kind of screening that ensures the rapid (within 3–5 min) identification of the number of impurities in samples of chemical products and their integer molecular weights.

CONCLUSIONS

In studying a sample of methyl methacrylate, a combination of chromatodistillation with APPCIMS made it possible to register characteristic m/z values corresponding to the expected molecular weights of 33 compounds. This number is noticeably higher than the number of impurities permissible in MMA according to *GOST 20370-74* (eight substances) [8]. An advantage of the proposed approach to the determination of impurities in high-purity methyl methacrylate is a possibility of recording the corresponding analytical signals (m/z) against the background of the main component. At that, the main component not only does not interfere with the registration, but also plays an important role (reagent substance) in creating conditions for the photochemical ionization of the desired substances under atmospheric pressure and increasing the sensitivity of their determination.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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