

STUDIES OF VOLATILE ORGANIC COMPOUNDS EMISSION FROM FRAGARIA VESCA AND FRAGARIA ANANASSA USING PROTON TRANSFER REACTION MASS SPECTROMETRY*

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Volatile organic compounds emission from wild strawberries (*Fragaria vesca*) and garden strawberries (*Fragaria ananassa*) were studied using the Proton Transfer Reaction Mass Spectrometry (PTR-MS). The samples of wild and garden strawberries were picked from the different regions in Poland (Pomerania and Mazovia). Mass spectra for all studied samples are presented in this work. Some organic compounds were identified based on the obtained spectra for samples of *Fragaria vesca* and *Fragaria ananassa* from different regions. Some differences between the mass spectra were found and discussed in the work.

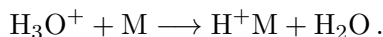
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1. Introduction

The problem of ionization of a sample substance is the main issue in mass spectrometry. There are a lot of ionization methods applied for this purpose. However, some of these methods may cause fragmentation of molecules. For example, Electron Ionization (EI) [1], Fast Atom Bombardment (FAB) [2] or ions bombardment (Secondary Ion Mass Spectrometry, SIMS) [3], Inductively Coupled Plasma (ICP) [4] are among methods which may lead to fragmentation of studied compounds. In the case of samples containing one chemical compound, fragmentation is even helpful in its characterization due to occurring a specific set of fragments. At the same time, when a research focuses on a mixture of various compounds, especially organic, the fragmentation greatly complicates their identification and study, and in some cases, it may completely prevent it.

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Among methods, that limit fragmentation of molecules, there is the Chemical Ionization (CI). This method uses various reagent gases (*e.g.*, CH₄, NH₃, C₄H₁₀) to primary ions formation which, in turn, ionizes the molecules of interest. The Proton Transfer Reaction Mass Spectrometry (PTR MS) is one of these CI methods. It produces H₃O⁺ hydronium ions, interaction of which with the test substance in a gaseous state leads to a proton transfer to the molecule M according to the following reaction:



The condition for this reaction is that the proton affinity of the studied molecules is higher than the proton affinity of water molecules [5–7].

The PTR-MS method has found many applications in environmental protection, medicine, biology and quality control of food products [8–12].

In this work, the PTR-MS approach has been applied to study of volatile organic compounds which are emitted from fruits of woodland strawberry (*Fragaria vesca*) and garden strawberry (*Fragaria ananassa*).

The main purpose of the work is to examine whether it is possible to identify the origin of fruits based on mass spectra obtained by the PTR-MS technique.

2. Materials and method

The samples of woodland strawberries were picked from the forest near Słupsk (Central Pomerania, Poland) and from the backyard garden in Słupsk in period of June 2019.

The samples of garden strawberries were picked from the strawberry plant in Mazovia region in the mid-north-eastern Poland and from the strawberry plant in Central Pomerania region in the northern Poland in period of July 2019.

In each case, the four fruit samples were analysed by PTR-MS in no more than 24 hours after harvest (strawberries from Mazovia were transported overnight in the cooled atmosphere). All studied samples had the same mass (about 100 g) and they have been contained in glass vessels (250 ml) covered with an aluminium foil. Capillary inlet tube was placed inside the glass vessel (with the fruit sample) through the small hole in the cover foil. All measurements were performed at room temperature (about 21°C).

The High Sensitivity model of PTR-MS apparatus with quadrupole analyser (mass range of 0–12 amu, resolution < 1 amu) was manufactured by IONICON (Innsbruck, Austria). Details of the construction have been described *e.g.* in works [13, 14]. In short, the apparatus is made of three main parts: ion source, drift chamber and analyzer. The ion source is a hollow cathode in which water vapour ionizes. As a result of ionization, during

a series of ionic reactions, protonated $\text{H}^+(\text{H}_2\text{O})_n$ water clusters with n up to several are generated [15, 16]. The dominant ions are hydronium ions, which are transported to the drift chamber. A sample of the tested gas is also transferred to this chamber through the capillary. The drift chamber consists of a series of annular electrodes that produce a homogeneous electric field. In this field, hydronium ions are accelerated and in collisions with neutral gas molecules, a proton transfer reaction occurs, described in the introduction. Then MH^+ ions pass to the quadrupole analyzer. In the presented experiment, both the capillary and the drift chamber were heated to 60°C to reduce gas condensation processes. The vacuum system consists of three differential turbo molecular pumps. In the ion detection area, the pressure was 10^{-5} mbar. The pressure in the drift chamber was 2.2 mbar and the drift voltage was 600 V.

3. Results

Mass scanning was performed in the range of 21 to 300 m/z (mass 21 corresponds to the $\text{H}^+\text{D}_2\text{O}$ hydronium ion isotope). Six mass scans and three background scans were performed for each sample. Background mass spectra did not deviate from the norm, *i.e.* they contained small amounts of *e.g.* acetone (a product of human metabolism) and a signal from ions that are formed in an ion source, *e.g.* O_2^+ , NO^+ or $\text{H}^+(\text{H}_2\text{O})_2$ (protonated water dimer), which in all cases were about the same level. A typical background mass spectrum is presented in Fig. 1. Because this work presents just comparative studies, the background signal was not subtracted from the sample signal. No ions were recorded for $m/z > 180$, neither for strawberries nor wild strawberries. For these reasons, the charts only show masses in the range from 40 to 180 m/z .

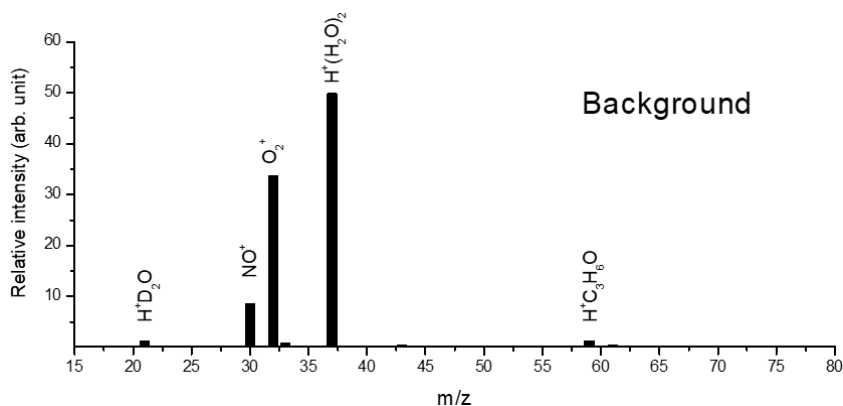


Fig. 1. Typical background PTR mass spectrum.

Mass spectra of wild strawberries (*Fragaria vesca*) collected in the forest and in the garden are compared in Fig. 2: we show results for only two samples of each kind, as the difference between samples of the same kind of strawberries were not significant and the obtained mass spectra could be regarded as identical for the same samples. Both for wild strawberries collected in the forest and in the garden, the spectra are repeatable for all four samples. In both cases, the strongest signals come from masses 43, 45, 61, 89 and 117. In the case of wild strawberries from the forest, it can be seen that the signal from ions with a mass of 171 amu is clearly stronger than for wild strawberries grown in a home garden. It can also be seen that there are repetitive differences in signal strength ratios, *e.g.* between masses 89 and 117 amu. For wild strawberries from the forest, ions weighing 89 amu are more numerous than those weighing 117, and in the case of strawberries from the garden, the opposite is true.

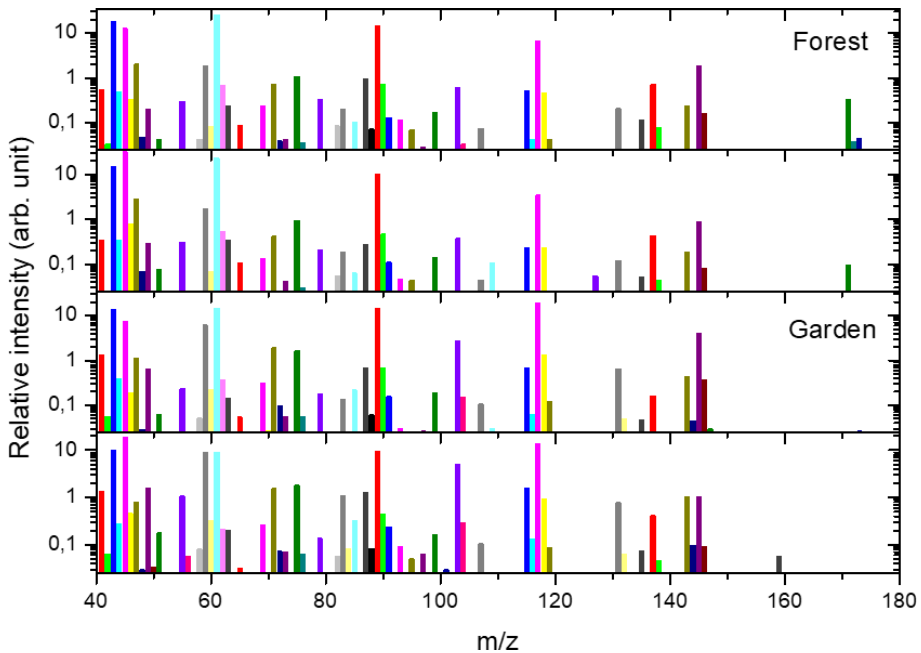


Fig. 2. Comparison of PTR mass spectra of wild strawberries collected in the forest and from a home garden — two samples of each kind are only shown.

For strawberries (*Fragaria ananassa*) from Mazovia and Central Pomerania, it can be stated that the results are also repeatable (Fig. 3). However, it is harder to notice the differences in this case, although in the mass spectrum of strawberries from Pomerania, ions with a mass of 145 amu are slightly more numerous than for strawberries from Mazovia.

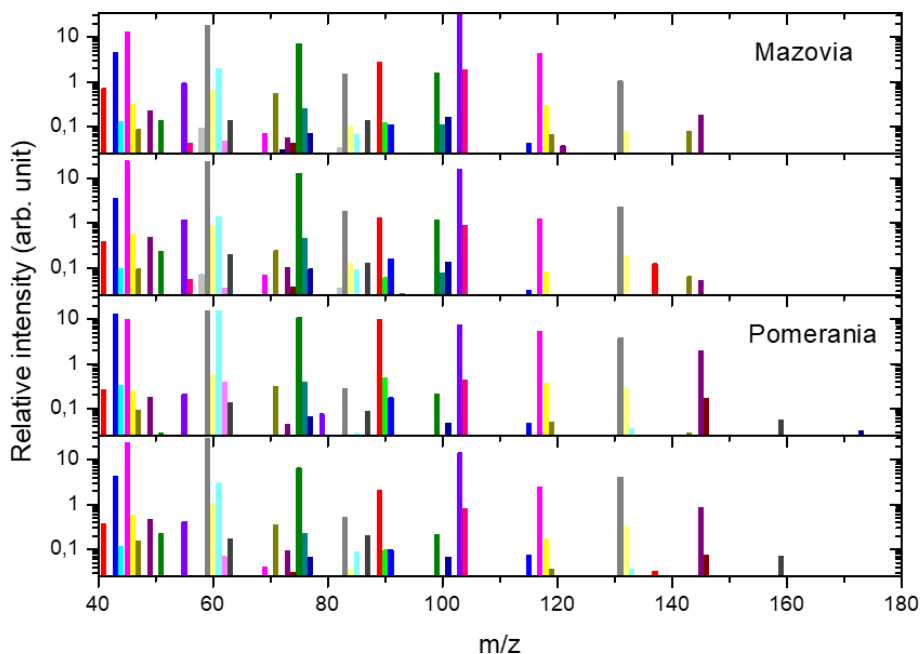


Fig. 3. Comparison of PTR mass spectra of strawberries collected in Mazovia and Pomerania.

As far as the differences between different samples of the same type of strawberries were only slight, present data indicate that it is possible with the PTR-MS to distinguish between wild and garden strawberries, and possibly, also their origin. In general, it can be stated that a more advanced statistical analysis is needed to identify different fruit origins of the same species. This requires testing more samples.

Identification of organic compounds by means of mass spectrometry is difficult, because the same masses may correspond to several dozen, and in the case of large masses, even several hundred chemical compounds. The quadrupole mass spectrometer has a low resolution, but even in the case of high resolution spectrometers, it is not possible to identify compounds that are built of the same atoms, but with different geometrical configurations (isomers). Therefore, in this work, preliminary identification of chemical compounds was made based on literature data obtained by chromatographic methods [17, 18] and using the NIST Chemistry WebBook and PubChem databases. The table below presents the results of such identification for the most abundant ions. In some cases, we offer more than one chemical compound for the same mass. It should be remembered that in fact one of the compounds or a mixture thereof may be emitted from the samples.

TABLE I

Identification of volatile organic compounds from PTR-MS spectra of wild and garden strawberries.

<i>m/e</i>	Compound	Formula	Peak color
41	Common fragment	$C_3H_5^+$	red
43	Common fragment	$C_3H_7^+$	blue
	Common ester fragment	$C_2H_3O^+$	
45	Acetaldehyde	$H^+C_2H_4O$	magenta
57	Dehydrated fragment	$C_4H_9^+$	purple
61	Acetic acid	$H^+C_2H_4O$	LT cyan
65	Common fragment	$C_5H_9^+$	red
71	Dehydrated fragment of alcohol, Propiolic acid	$C_5H_{11}^+$ $H^+C_3H_2O_2$	dark yellow
75	Propiolic acid	$H^+H_3H_6O_2$	olive
87	Pentanal	$H^+C_5H_{10}O$	dark gray
	Isovaleraldehyde	$H^+C_5H_{10}O$	
89	n-Pentanol	$H^+C_5H_{12}O$	red
	Propane, 1-methoxy-2-methyl- trans-2-Hexenal	$H^+C_6H_{10}O$	olive
101	cis-3-Hexenol, trans-2-Hexenol, Hexanal	$H^+C_6H_{12}O$	dark cyan
103	Methyl butanoate	$H^+C_5H_{10}O_2$	violet
107	Benzaldehyde	$H^+C_7H_6O$	light gray
115	Heptanal	$H^+C_7H_{14}O$	blue
117	Hexanoic acid, Ethyl butanoate Butyl acetate, Methyl-2-methylbutanoate	$H^+C_6H_{12}O_2$	magenta
131	Ethyl-2-methylbutanoate, 2-Methylbutyl acetate, 3-Methylbutyl acetate (Isoamyl acetate), Methyl hexanoate	$H^+C_7H_{14}O_2$	gray
137	Limonene, Fragment of linalyl acetate	$H^+C_{10}H_{16}$	red
143	Nonanal, trans-2-Hexenyl acetate, cis-3-Hexenyl acetate, Mesifurane	$H^+C_9H_{18}O$ $H^+C_8H_{14}O_2$	dark yellow
145	Butyl butanoate, Ethyl hexanoate, Hexyl acetate	$H^+C_7H_{10}O_3$ $H^+C_8H_{16}O_2$	purple
171	delta-, gamma-Decalactone, trans-2-Hexenyl butanoate	$H^+C_{10}H_{18}O_2$	olive
173	Octyl acetate	$H^+C_{10}H_{20}O_2$	roval

The ion with the mass $m/z = 171$, in our data observed only for wild strawberries, could correspond to gamma-Decalactone, already known to be present in the flavour of peach and strawberries. It is also possible that PTR induces fragmentation of heavier fragments, so we have not observed ions above $m/z = 173$. Reconstruction of the parent molecule from fragments is difficult, and the application of theoretical models to check their stability is both time-consuming and ambiguous, see [16].

4. Summary

The paper presents the results of research on emissions of volatile organic compounds (VOC) from wild strawberries (*Fragaria vesca*) and strawberries (*Fragaria ananassa*) from various sources. Preliminary VOC identification was made. It was shown that the conducted analysis could be a good starting point for the development of PTR-MS based methods to identify place of origin not only of strawberries, but also of other fruits with relatively intensive VOCs emission. However, it should be noted that there are a lot of factors that could lead to deviations in chemical compositions of plants. Among them are not only place of origin, but also weather conditions in a given year, types of fertilizers and insecticides used in agriculture, *etc.* For this reason, these facts should also be taken into account in further researches. For strawberries from Pomerania and Mazovia, mass spectra are similar, while wild strawberries from garden and forest show bigger differences. Organoleptic examination showed that the wild strawberries from forest were the most aromatic: this would correspond to the presence of heaviest ($m/z = 171$) ions in mass spectra. In turn, the wild strawberries from garden were the sweetest. To make the PTR technique useful for the identification of the origin (and the state of conservation) of strawberries, there is a need to test more samples and to use advanced statistical methods to identify VOC. Unfortunately, we must wait till a next summer season.

The idea of measuring PTR mass spectra of strawberries was originally formulated with prof. G. Karwasz, at that time at the Słupsk Pomeranian Academy, see our internet didactical notes [20, 21].

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