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3 **Magnetic scavengers as carriers of analytes for the flowing atmospheric**
4 **pressure afterglow mass spectrometry (FAPA-MS)**
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48
49 **Abstract**
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51 In this paper, a procedure for the preconcentration and transport of the mixtures of
52 acids, bases, and drug components to the mass spectrometer using magnetic scavengers is
53 presented. Flowing atmospheric pressure afterglow mass spectrometry (FAPA-MS) was used
54 as an analytical method for identification of the compounds by thermal desorption from the
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3 scavengers. The proposed procedure is fast and cheap, and does not involve time-consuming
4 purification steps. The developed methodology can be applied for trapping harmful
5 substances in minute quantities, to transport them to the specialized, remotely located
6 laboratory.
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11 12 13 **Keywords**

14 magnetic scavengers, ambient plasma, mass spectrometry, thermal desorption, analysis
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20 21 **1. Introduction**

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24 Magnetic materials are common in numerous applications in biology, analytical
25 chemistry or biochemistry.^{1, 2} Magnetic field is a force used for isolation and separation of
26 desired molecules. Particularly, magnetic iron oxide (Fe_3O_4 magnetite and $\gamma\text{-Fe}_2\text{O}_3$
27 meghemite) nanoparticles are often applied, because of their superparamagnetic properties.³
28 Such approach significantly facilitates separation process, as the molecules are attached to the
29 magnetic particles and can easily be separated from complex mixtures. The scavengers
30 prepared in such a way do not retain residual magnetism after removal of the field. The
31 nanoparticles are also characterized by high dispersibility, very good adsorption capacity, and
32 a variety of surface modifications is possible. The latter feature is of importance because the
33 magnetic core has a tendency to form large aggregates of different magnetic properties.
34 Several methods have been applied for coating the magnetic core. One of the commonly used
35 procedures includes silica coating, followed by further modifications with silane agents
36 bearing functional groups. The presence of the shells with specific functional groups provides
37 better stability of the magnetic material and also offers selectivity toward desired compounds.
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55 Such material can effectively isolate harmful substances⁴⁻⁶ or participate in targeted
56 drug delivery.^{7, 8} Very popular silica-coated magnetic nanoparticles, functionalized by *e.g.* γ -
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3 mercapto-, and γ -aminopropyltriethoxysilane, poly(amidoamine) (PAMAM) dendrimers and
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5 polyethylene imine (PEI) polymers, surfactants, and hyaluronic acid, can be used for separation
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7 and concentration of trace amounts of heavy metals.⁹⁻¹¹ Magnetic sorbents can be applied for
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9 the solid phase extraction of many pollutants present in environmental^{12, 13} or biological
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11 samples.¹⁴
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14 One of the ionization methods used in the analysis of components in various complex
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16 matrices is flowing atmospheric pressure afterglow (FAPA).¹⁵⁻¹⁹ FAPA is a method that
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18 instantaneously ionizes gases, liquids, and solids under ambient conditions. This technique
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20 ionizes compounds, introduced into the source, regardless of the physical state and the
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22 presence of impurities.^{20, 21} Thermal evaporation of the analyte from the investigated material
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24 and its introduction into the stream of primary ions, allows for detailed examination of the
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26 samples without pre-treatment.
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30 The ability for selective extraction of the compounds from the matrix using magnetic
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32 scavenger is determined by its functional groups. Complex formation between the functional
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34 group on the surface of the scavenger and the analyte, significantly increases concentration of
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36 the substance to the measurable level, and also enables its transport to the remotely located
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38 analytical facility. Ions, generated with the aid of thermal desorption, may be directly
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40 introduced into the plasma stream and rapidly identified in the mass spectrometer. In this
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42 paper, we present a procedure for the determination of various components using
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44 functionalized magnetic scavengers and FAPA mass spectrometry, as a robust, analytical
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46 method. The proposed approach is fast and cheap, and omits time-consuming purification
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48 steps.
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51 52 53 54 **2. Experimental**

55 56 57 *2.1 Materials*

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3 All reagents used are commercial products. Scavengers, magnetic carboxy-
4 functionalized microparticles, denoted as $\text{Fe}_3\text{O}_4\text{-R-COOH}$, and magnetic amino-
5 functionalized, denoted as $\text{Fe}_3\text{O}_4\text{-R-NH}_2$, (BioMag[®] Plus Particles) were obtained from
6 Sigma-Aldrich (St. Louis, MO, USA). Magnetic scavengers consisted of an iron oxide core
7 with silane coating. BioMag[®] Plus Particles are approx. 1 micron diameter with particle mass
8 concentration of 18-22 mg mL^{-1} (water solution). For the studies, we used three groups of
9 analytes: acids (benzoic, caffeic, malic, quinic, and phthalic acids), bases (nicotine, sparteine,
10 and polyamines), and a commonly used analgesic consisting of paracetamol, propyphenazone,
11 and caffeine. All analytes were obtained from Sigma-Aldrich (St. Louis, MO, USA) except
12 analgesic, which was obtained from a local pharmacy store. Structures of all analytes are
13 presented in Fig. 1. All solvents of the purity grade (p.a.), were obtained from POCH
14 (Gliwice, Poland) and were used without further purification.

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30 Ferrite magnets (ENES Magnesy, Warsaw, Poland) were of diameter 8 ± 0.2 mm and
31 height 5.0 ± 0.1 mm. Magnetic properties of the ferrite magnets: induction remanence (Br)
32 min. 0.37 T, coercion (HCB) min. 175 kA m^{-1} , coercivity (HcJ) min. 180 kA m^{-1} , magnetic
33 energy density $(\text{BH})_{\text{max}}$ min. 26 kJ m^{-3} . Curie temperature is around 450 °C. A new magnet
34 was used for each experiment.

35 36 37 38 39 40 41 42 *2.2 Preparation of sample solutions*

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45 A series of water or methanol solutions was prepared: benzoic and caffeic acids
46 (sample 1), malic and quinic acids (sample 2), phthalic acid (sample 3), nicotine and sparteine
47 (sample 4), diethylenetriamine, triethylenetetramine, tetraethylenepentamine and
48 pentaethylenhexamine (sample 5). The concentration of each analyte in solution was *ca.* 1
49 mM. The analgesic tablet was dissolved in 10 mL of methanol.

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52 For determination of the detection limit, a series of methanol solutions of benzoic acid
53 10^{-4} , 10^{-5} , 10^{-6} and 10^{-7} M were prepared.

2.3 Adsorption of the analytes on magnetic scavengers

To 10 mL of an appropriate sample solution, 10 mg (0.5 mL) of the suspension of magnetic scavengers have been added. To samples 1-3, containing acidic compounds, a suspension of Fe₃O₄_R_NH₂ has been added, whereas to samples 4 and 5, containing bases, a suspension of Fe₃O₄_R_COOH has been added. For the determination of detection limit, a suspension of Fe₃O₄_R_NH₂ has been added to 10 mL of benzoic acid solution at each concentration examined. After 10 min. of stirring, ferrite magnet attached to a holder was introduced into the solution for magnetic separation of the scavengers. After collecting all magnetic scavengers, the ferrite magnet was removed from the solution and immersed in deionized water to remove impurities and nonspecifically attached material, *e.g.* residual droplets of the solution. After thorough washing with deionized water, the ferrite magnet was placed in the programmable heater, which was located below the FAPA plasma stream (Fig. 2). During heating, the analytes were gradually desorbed, depending on their volatility, and directly introduced into the plasma stream, followed by their subsequent identification in the mass spectrometer.

2.4 Instrumentation

Estimation of the weight loss of the magnetic scavengers with the analytes adsorbed was conducted in a thermal gravimetric analyzer (Setsys 1200, Setaram, Caluire, France) under helium atmosphere from 20 to 600 °C at a heating rate of 10 °C min⁻¹.

A Bruker Esquire 3000 quadrupole ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) was used for all measurements. The typical electrospray ionization (ESI) source settings were found to be optimal also for the FAPA ion source, with the exception of the mass spectrometer entrance glass capillary voltage, where lower potential (1 kV) compared to the standard ESI setting (4.5 kV) was used. The temperature of the glass

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3 capillary was set to 200 °C; the drying gas flow was maintained at 3 L min⁻¹, and the
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5 nebulizing gas (N₂) was not applied. The scan range was set from 80 to 500 *m/z*. For tandem
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7 MS/MS experiments the isolation width was set to 2 *m/z* and the fragmentation amplitude was
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9 in the range of 0.5 to 0.8 units. Mass spectra of the compounds desorbed from Fe₃O₄_R_NH₂
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11 scavengers were recorded in the negative ion mode, whereas mass spectra of the compounds
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13 desorbed from Fe₃O₄_R_COOH scavengers were recorded in a positive ion mode.
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17 A NOVA011 (ERTEC, Wrocław, Poland) flowing atmospheric-pressure afterglow
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19 plasma source was used for the ionization of all samples. Construction of the FAPA source
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21 was described elsewhere.¹⁷ Shortly, the outlet of the device was mounted approximately 5 cm
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23 from the inlet of a mass spectrometer at horizontal position. Helium, as a discharge gas, was
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25 continuously delivered at a flow rate of 1.0 L min⁻¹. The heating system with a programmable
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27 temperature from 20 to 300 °C was used for thermal desorption of the analytes from the
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29 magnetic scavengers. The heater was elongated with the metal holder allowing for fast
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31 mounting of the removable ferrite magnet. The holder with ferrite magnet was placed 1 cm
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33 below the plasma stream.
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37 Evaluation of the detection limit was based on the ion chromatograms of benzoic acid
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39 solutions. 10 μL of each solution (concentration described above) were introduced into the
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41 electrically heated mini crucible. Afterwards, the solution was instantly evaporated to allow
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43 fast introduction of vapors into the plasma stream.
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46 47 **3. Results and discussion**

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49 Functionalized, magnetic scavengers applied in this work, comprise a group of
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51 materials decorated with carboxy-, or amino - terminal groups on the surface. Such structures,
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53 added to a solution of acidic or basic compounds, lead to the attachment of analytes on the
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55 surface of insoluble particles. Stable complexes, formed by noncovalent, hydrogen bonds,
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3 enable preconcentration of the samples on the surface of the magnetic carriers. The resulting
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5 complexes are dissociated by applying temperature gradient, and the rate of desorption
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7 depends on the strength of the hydrogen bonds, and therefore on the nature of an analyte.
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9 Photographs of the subsequent stages of the described analytical procedure are presented in
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11 Fig. 2. The complexes formed between functionalized surfaces and adsorbed compounds,
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13 were stable for at least one month at ambient temperature.
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16 17 3.1 Thermal stability of the scavengers 18 19

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21 Thermal stability of $\text{Fe}_3\text{O}_4\text{-R-COOH}$ and $\text{Fe}_3\text{O}_4\text{-R-COOH}$ with noncovalently bound
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23 basic compounds was tested. TGA curves for magnetic $\text{Fe}_3\text{O}_4\text{-R-COOH}$ without (**a**) and with
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25 noncovalently bound sparteine (**b**) or tetraethylenepentamine (**c**), are shown in Fig. 3. The
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27 early weight loss of $\text{Fe}_3\text{O}_4\text{-R-COOH}$ (Fig. 3a), observed below 220 °C, can be attributed to
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29 the removal of physically adsorbed water molecules. Further weight loss (above 300 °C)
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31 corresponds to the decomposition and subsequent vaporization of coating layer with
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33 functional groups, attached to the particles' surface (-R-COOH). The inorganic, magnetic core
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35 (Fe_3O_4) shows excellent thermal stability up to 600 °C. TGA curves of $\text{Fe}_3\text{O}_4\text{-R-COOH}$ with
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37 noncovalently bound amines show the obvious initial mass loss in the temperature region
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39 (below 300 °C) close to the boiling-, or decomposition points of an attached amine (Figs. 3b
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41 and 3c). In addition, the weight loss for the linear amine (tetraethylenepentamine) was about
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43 twice as high as for sparteine, thus suggesting greater accessibility of the functional groups on
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45 the surface. Other linear amines demonstrate similar behavior. Summarizing, it can be
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47 concluded that the total weight loss at 600 °C is approx. 5 wt%, 10 wt%, and 20 wt% for
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49 $\text{Fe}_3\text{O}_4\text{-R-COOH}$ particles alone, $\text{Fe}_3\text{O}_4\text{-R-COOH}$ with sparteine, and $\text{Fe}_3\text{O}_4\text{-R-COOH}$ with
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51 tetraethylenepentamine, respectively.
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57 3.2 Mass spectrometric identification of the analytes thermally desorbed from $\text{Fe}_3\text{O}_4\text{-R-NH}_2$ 58 59 60

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3 The extracted ion chromatograms of benzoic (red line) and caffeic (blue line) acids,
4 along with their FAPA-MS spectra, are presented in Fig 4. Inspection of these chromatograms
5 shows that an increasing temperature consecutively releases benzoic acid, followed by caffeic
6 acid. This observation has been confirmed by recording mass spectra at different time
7 intervals. Mass spectrum obtained after 1.6 min. from the beginning of the experiment shows
8 one major signal at m/z 121, corresponding to benzoate ion. Mass spectrum obtained after 3.3
9 min. shows high intensity signal at m/z 121 and a small signal at m/z 179, corresponding to
10 caffeate ion. Mass spectrum acquired after 4.8 min. shows abundant signal at m/z 179. The
11 weak signal at m/z 135 probably corresponds to decarboxylated caffeic acid.²²

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14 Fig. 5 shows MS and MS/MS spectra of malic (m/z 133) and quinic (m/z 191) acids. In
15 contrast to the analysis of a mixture of benzoic and caffeic acids, malic and quinic acids were
16 not well separated during thermal desorption. No obvious differences in intensities of the ions
17 corresponding to these compounds were observed on the extracted ion chromatograms (data
18 not shown). Despite the lack of separation by thermal desorption, additional analysis in the
19 MS/MS mode allowed for thorough identification of both components.

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22 MS and MS/MS spectra of phthalic acid are presented in Fig. 6. Because there was
23 only one analyte in the solution, the very good quality spectrum has been recorded. To
24 examine whether the signal at m/z 121 corresponds to decarboxylation of phthalic acid or
25 belongs to contaminant, an additional MS/MS analysis was performed. Appearance of this
26 signal in the MS/MS mode proves that its origin can be contributed to decarboxylation of
27 phthalic acid. This observation is in accordance with literature, describing signal that appears
28 during chemical ionization of phthalic acid.²³

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3.3 Mass spectrometric identification of the analytes thermally desorbed from

Fe₃O₄_R_COOH

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3 The extracted ion chromatograms of nicotine (red line) and sparteine (blue line), along
4 with their FAPA-MS spectra, are shown in Fig. 7. Similarly to the analysis of a mixture of
5 benzoic and caffeic acids, thermal desorption generated by temperature gradient allows for the
6 separation of analytes by their consecutive release. At the beginning of the experiment, the
7 signal corresponding to nicotine (m/z 163) has high intensity, whereas the ion related to
8 sparteine (m/z 235) has its intensity *ca.* ten times lower. This is represented by the spectrum
9 obtained after 1.1 min. from the beginning of the experiment. While the temperature rises, the
10 intensities of these two signals become almost equal (spectrum after 1.5 min.; Fig. 7). After
11 1.8 min., the intensity of a signal corresponding to sparteine becomes around five times higher
12 than the intensity of a signal corresponding to nicotine. Ultimately, after 2.2 min., the signal at
13 m/z 235 is the only one present on the spectrum.
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27 Fig. 8 shows FAPA-MS spectra of a mixture of diethylenetriamine (m/z 104),
28 triethylenetetramine (m/z 147), tetraethylenepentamine (m/z 190), and pentaethylenehexamine
29 (m/z 233). After 1.7 min. from the beginning of the experiment, the signals corresponding to
30 diethylenetriamine and triethylenetetramine are observed on the spectrum. However, the most
31 intense signals on this spectrum correspond to contaminants. After 2.2 min., the signal at m/z
32 104 disappears, whereas the ion corresponding to tetraethylenepentamine can be observed.
33 After 3.3 min., the signal belonging to triethylenetetramine has a very low intensity, whereas
34 the most abundant ions on the spectrum derive from tetraethylenepentamine and
35 pentaethylenehexamine. These results clearly indicate that signal intensity is related to
36 volatility of particular compounds.
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49 FAPA-MS spectra of the components of the analgesic pill consisting of paracetamol
50 (m/z 152), caffeine (m/z 194), and propyphenazone (m/z 231) are shown in Fig. 9. The signal
51 origination from paracetamol is the only one visible on the spectrum recorded 2.2 min. from
52 the beginning of the experiment. The signal belonging to caffeine is observed on the spectra
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3 recorded after 2.2 and 2.7 min.. The signal corresponding to propyphenazone is detectable on
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5 all spectra, in which it has always the highest intensity, as compared to other drug
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7 components. This observation can be explained in two ways: propyphenazone has been
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9 adsorbed with the highest efficiency on the Fe₃O₄_R_COOH surface, or this compound can
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11 easily ionize.
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13 14 15 *3.4 Estimation of the limit of detection (LOD)*

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18 In order to estimate LOD, a series of experiments have been conducted, for which
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20 benzoic acid has been chosen as a model compound. Methanol solutions of benzoic acid at
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22 concentrations of 10⁻⁴; 10⁻⁵; 10⁻⁶, and 10⁻⁷ M have been prepared and subsequently analyzed
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24 directly by FAPA-MS or using preconcentration procedure described in this work. Direct
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26 analysis by FAPA-MS involved placement of the solution in an electrically heated mini
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28 crucible that allows rapid heating. The vapors were therefore introduced into the plasma
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30 stream in seconds, which ensures that the overall amount of benzoic acid that was present in
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32 the solution has been instantaneously ionized and introduced into the mass spectrometer. To
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34 estimate LOD of the preconcentration procedure, Fe₃O₄_R_NH₂ scavengers have been added
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36 to the benzoic acid solutions of each concentration. Subsequent heating with programmable
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38 heater caused gradual increase of desorption of benzoic acid from the scavenger that could be
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40 observed on the extracted ion chromatogram of benzoate ion. The results of LOD experiments
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42 are presented in Fig. 10. Every analytical instrument produces a signal even when a mixture
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44 without an analyte (reagent blank) is analyzed. In order to calculate LOD the intensity of this
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46 signal (referred to as the noise level) have to be measured. The average intensity of a signal at
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48 *m/z* 121 was calculated after ten measurements of this signal intensities obtained in absence of
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50 benzoic acid (pure methanol was used for measurements). Afterwards standard deviation of
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52 these ten measurements have been calculated. The value of average intensity summed with
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54 standard deviation multiplied by three was marked in Fig. 10 by the dashed red line. In
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3 accordance with the LOD definition ($\text{LOD} = \text{mean blank value} + 3 \times \text{standard deviation}$)²⁴, if
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5 the average intensity of signal at m/z 121 exceeds the value represented by this red line, than
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7 the analyte is within the detection range. For direct analysis by FAPA-MS, the LOD was
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9 estimated at 10^{-4} M, whereas for presented the developed preconcentration procedure, the
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11 LOD was estimated at 10^{-6} M. In all experiments, the average intensities of a signal at m/z 121
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13 were calculated from the extracted ion chromatograms from the time region where these
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15 intensities were the highest (average from ten measurements). The extracted ion
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17 chromatograms of the ion at m/z 121 obtained for pure methanol and for described
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19 preconcentration procedure for the lowest detectable concentration (10^{-6} M) of benzoic acid,
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21 are presented in Fig. 11.
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27 **4. Conclusions**

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29 The low-cost, small ferrite magnets with a high Curie temperature, allow for the rapid
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31 analysis of organic compounds released from the functionalized surfaces of the scavengers by
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33 thermal desorption, and detection using FAPA mass spectrometry.
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36 The idea to bind analytes on the surface of the functional magnetic scavengers to
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38 transport them to the remotely located mass spectrometry facility, allows for qualitative and
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40 analysis of a wide group of organic compounds using FAPA-MS. The analytical procedure
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42 for the determination of acidic or basic analytes not only allows for the effective
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44 preconcentration of trace amounts of the analytes (LOD was estimated at 10^{-6} M), but also
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46 enables for the safe storage of often harmful substances (*e.g.* warfare gases, toxins, narcotics,
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48 pesticides) during transportation to the laboratory. Moreover, the analytical procedure
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50 described in our work can be extended to a large variety of compounds, either acids or bases.
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52 Subsequent thermal desorption of the compounds, while introducing them to the plasma jet,
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54 which is a soft ionization technique, generates mass spectra of a very good quality.
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3 Additionally, careful adjustment of temperature gradient may serve as a preliminary
4 separation step during analysis of various mixtures. Low cost implementation of the magnetic
5 scavengers, high degree of concentration of the analyte on their surfaces, and easy transport
6 make the presented approach preferential to be considered as an alternative to other analytical
7 methods for the determination of dilute, organic compounds in liquid phase. Further chemical
8 modifications of the scavengers may lead to the higher selectivity of the system, capable of a
9 more discriminative capture of desired compounds.
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Figure captions

Fig. 1 The structures of all analytes examined.

Fig. 2 Photographs of the subsequent stages of analytical procedure described in the text.

Fig. 3 TGA curves: magnetic microparticles Fe₃O₄_R_COOH (a), Fe₃O₄_R_COOH with sparteine (b) and Fe₃O₄_R_COOH with tetraethylenepentamine (c).

Fig. 4 Extracted ion chromatograms of benzoic (red line) and caffeic (blue line) acids (a), along with FAPA-MS spectra of their mixture, thermally desorbed from Fe₃O₄_R_NH₂ after: 1.6 (b); 3.3 (c), and 4.8 (d) minutes from the beginning of the experiment.

Fig. 5 FAPA-MS spectra of malic and quinic acids thermally desorbed from the magnetic Fe₃O₄_R_NH₂ (a); MS/MS spectrum of malic acid (b); MS/MS spectrum of quinic acid (c).

Fig. 6 FAPA-MS spectrum of phthalic acid thermally desorbed from the magnetic Fe₃O₄_R_NH₂ (a); MS/MS spectrum of phthalic acid (b).

Fig. 7 Extracted ion chromatograms of nicotine (red line) and sparteine (blue line) (a), along with FAPA-MS spectra of their mixture thermally desorbed from Fe₃O₄_R_COOH after: 1.1 (b); 1.5 (c); 1.8 (d), and 2.2 (e) minutes from the beginning of the experiment.

Fig. 8 FAPA-MS spectra of diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenhexamine thermally desorbed from Fe₃O₄_R_COOH after: 1.7 (a); 2.2 (b), and 3.3 (c) minutes from the beginning of the experiment.

Fig. 9 FAPA-MS spectra of the components of the analgesic drug (paracetamol, caffeine, and propyphenazone), thermally desorbed from Fe₃O₄_R_COOH after: 2.2 (a); 2.7 (b), and 3.4 (c) minutes from the beginning of the experiment.

Fig. 10 Limit of detection (LOD); the LOD value (represented by the red dashed line) was calculated as an average signal intensity for reagent blank (methanol) plus three times standard deviation of the reagent blank's signal.

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3 **Fig. 11** Extracted ion chromatograms of the signal at m/z 121 obtained for pure methanol
4 (blue line) and for the developed preconcentration procedure for 10^{-6} M of benzoic acid (red
5 line).
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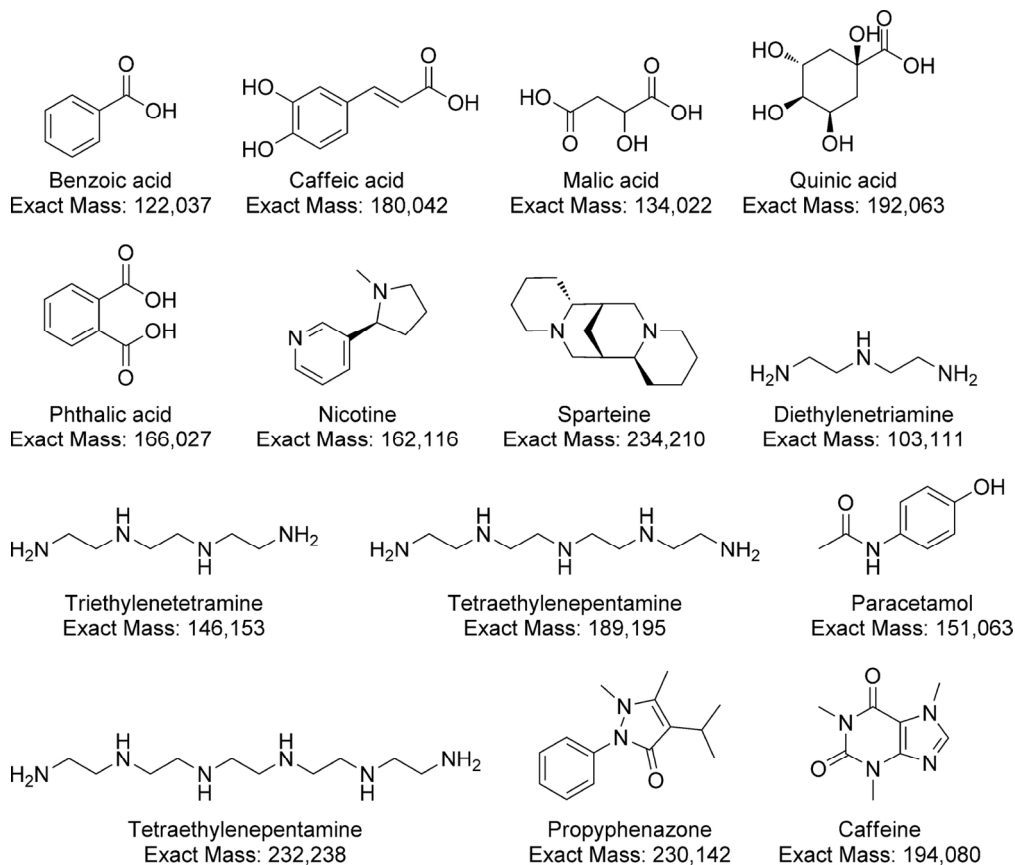


Fig. 1 The structures of all analytes examined.
70x60mm (600 x 600 DPI)

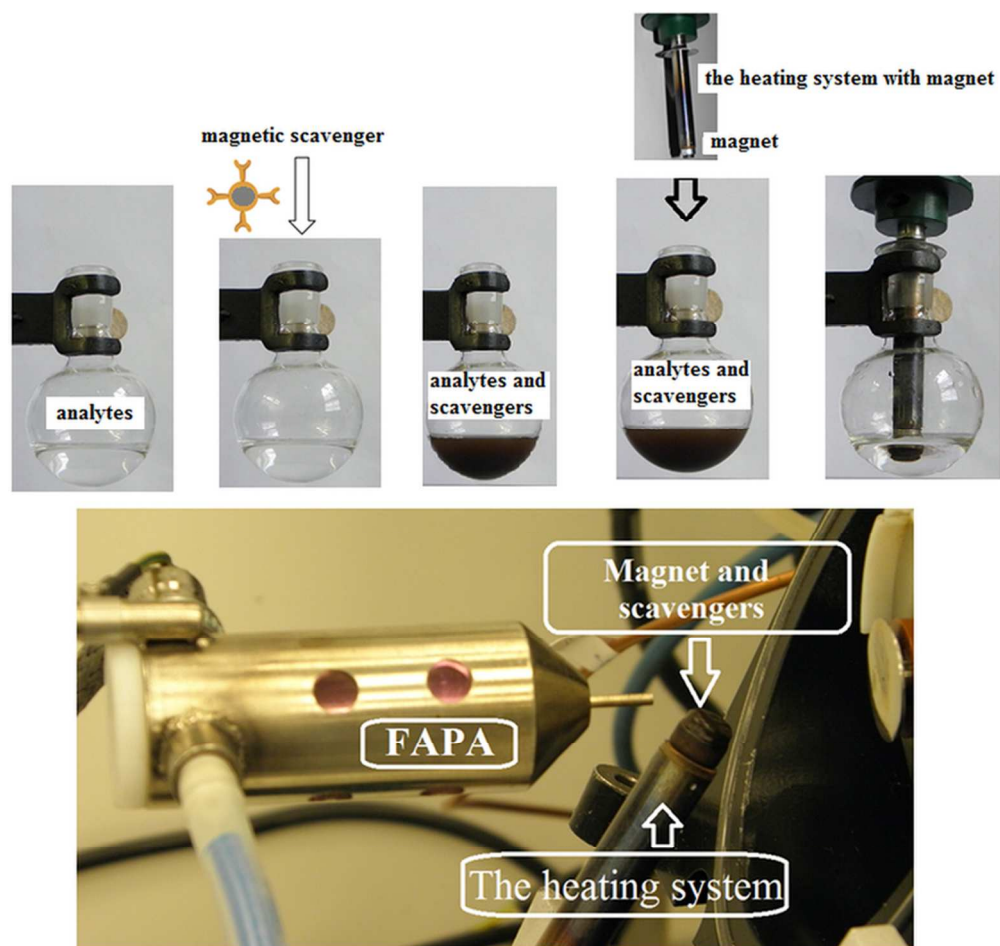


Fig. 2 Photographs of the subsequent stages of analytical procedure described in the text.
82x77mm (300 x 300 DPI)

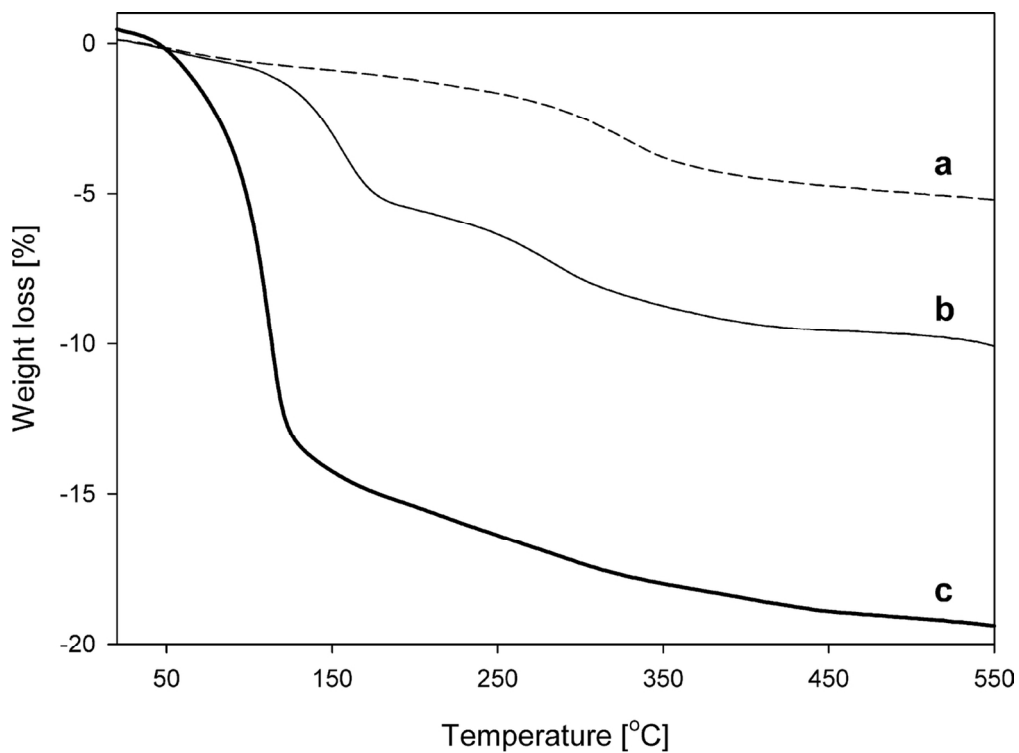


Fig. 3 TGA curves: magnetic microparticles Fe₃O₄_R_COOH (a), Fe₃O₄_R_COOH with sparteine (b) and Fe₃O₄_R_COOH with tetraethylenepentamine (c).
61x45mm (600 x 600 DPI)

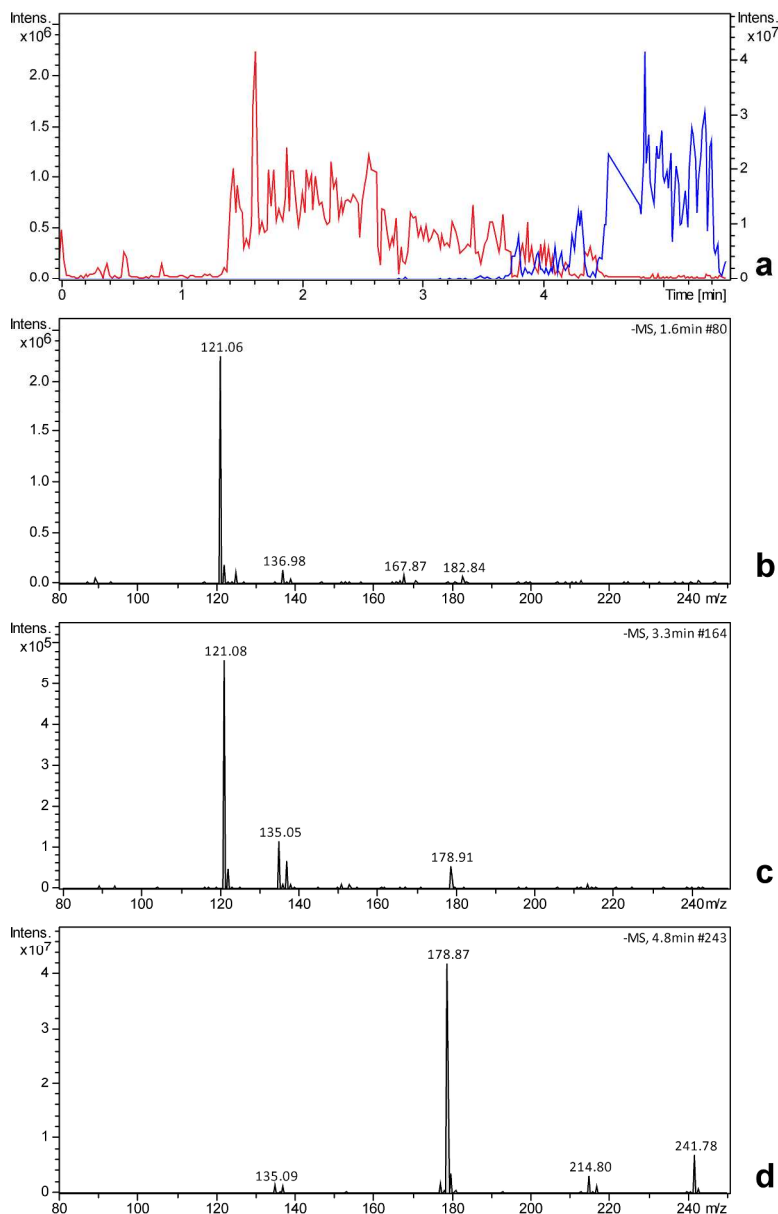


Fig. 4 Extracted ion chromatograms of benzoic (red line) and caffeic (blue line) acids (a), along with FAPA-MS spectra of their mixture, thermally desorbed from Fe₃O₄_R_NH₂ after: 1.6 (b); 3.3 (c), and 4.8 (d) minutes from the beginning of the experiment.
130x203mm (600 x 600 DPI)

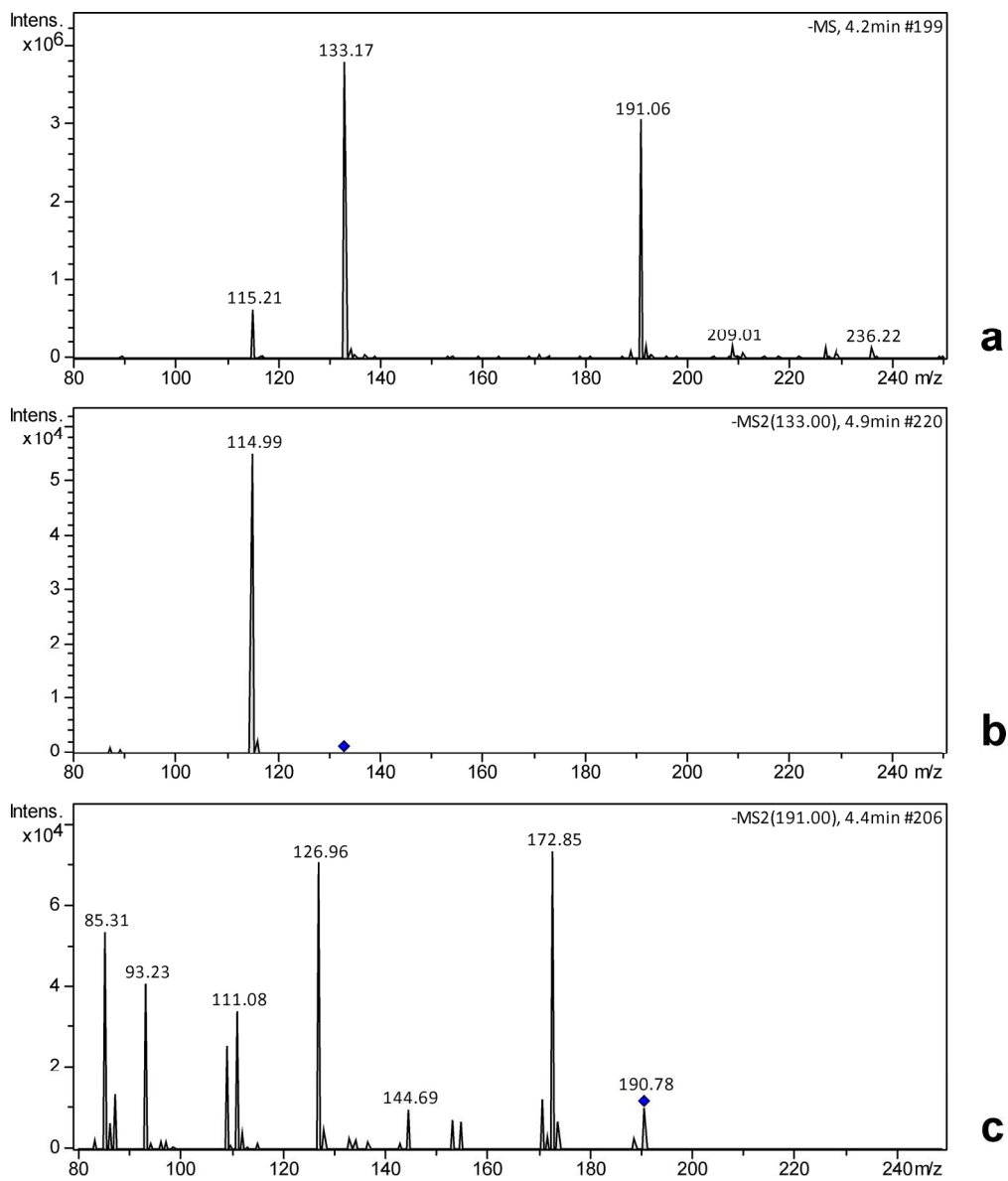


Fig. 5 FAPA-MS spectra of malic and quinic acids thermally desorbed from the magnetic Fe₃O₄-R-NH₂ (a); MS/MS spectrum of malic acid (b); MS/MS spectrum of quinic acid (c). 97x113mm (600 x 600 DPI)

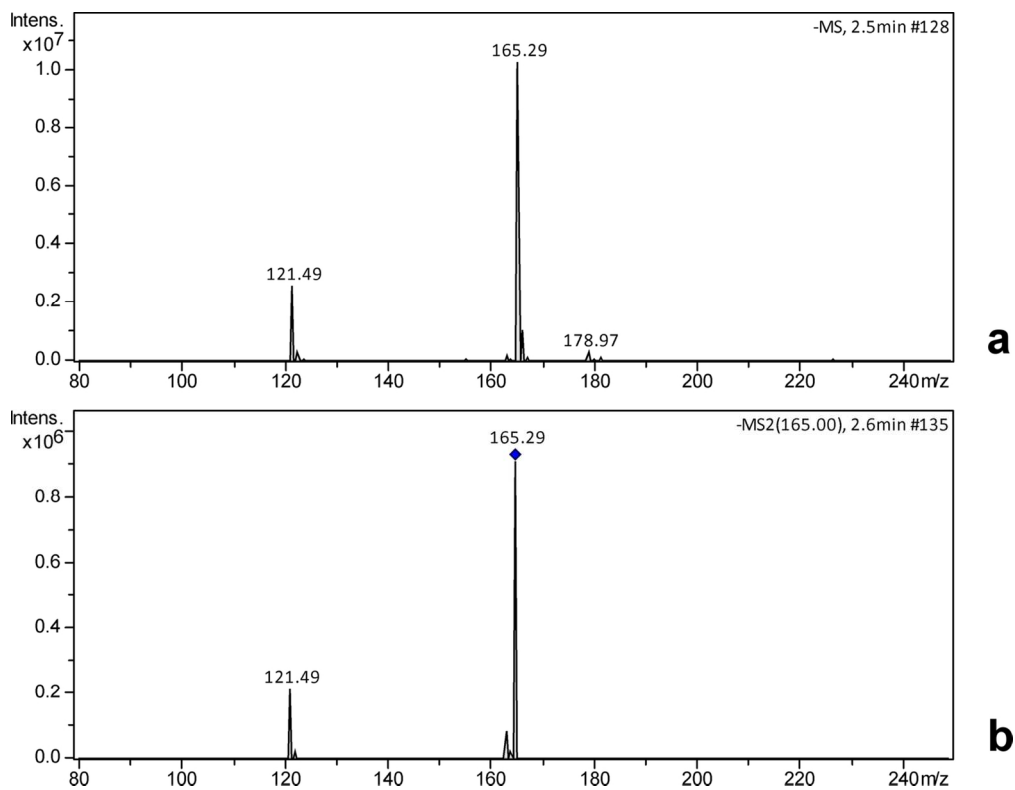


Fig. 6 FAPA-MS spectrum of phthalic acid thermally desorbed from the magnetic Fe₃O₄_R_NH₂ (a); MS/MS spectrum of phthalic acid (b).
64x49mm (600 x 600 DPI)

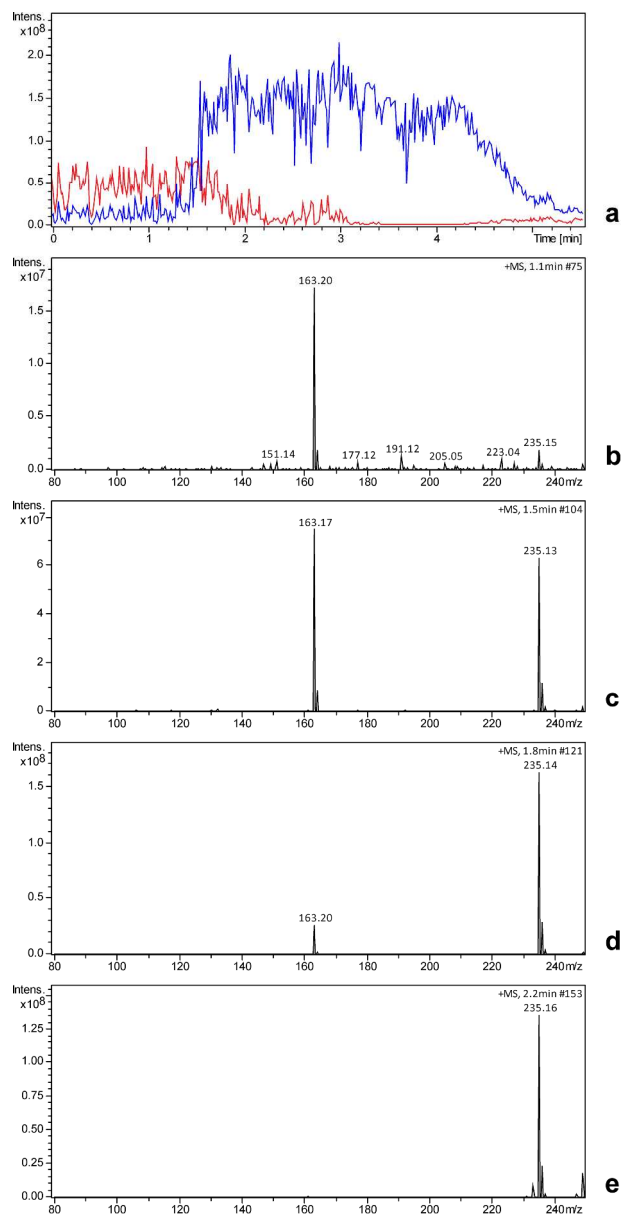


Fig. 7 Extracted ion chromatograms of nicotine (red line) and sparteine (blue line) (a), along with FAPA-MS spectra of their mixture thermally desorbed from Fe₃O₄-R-COOH after: 1.1 (b); 1.5 (c); 1.8 (d), and 2.2 (e) minutes from the beginning of the experiment.
163x323mm (600 x 600 DPI)

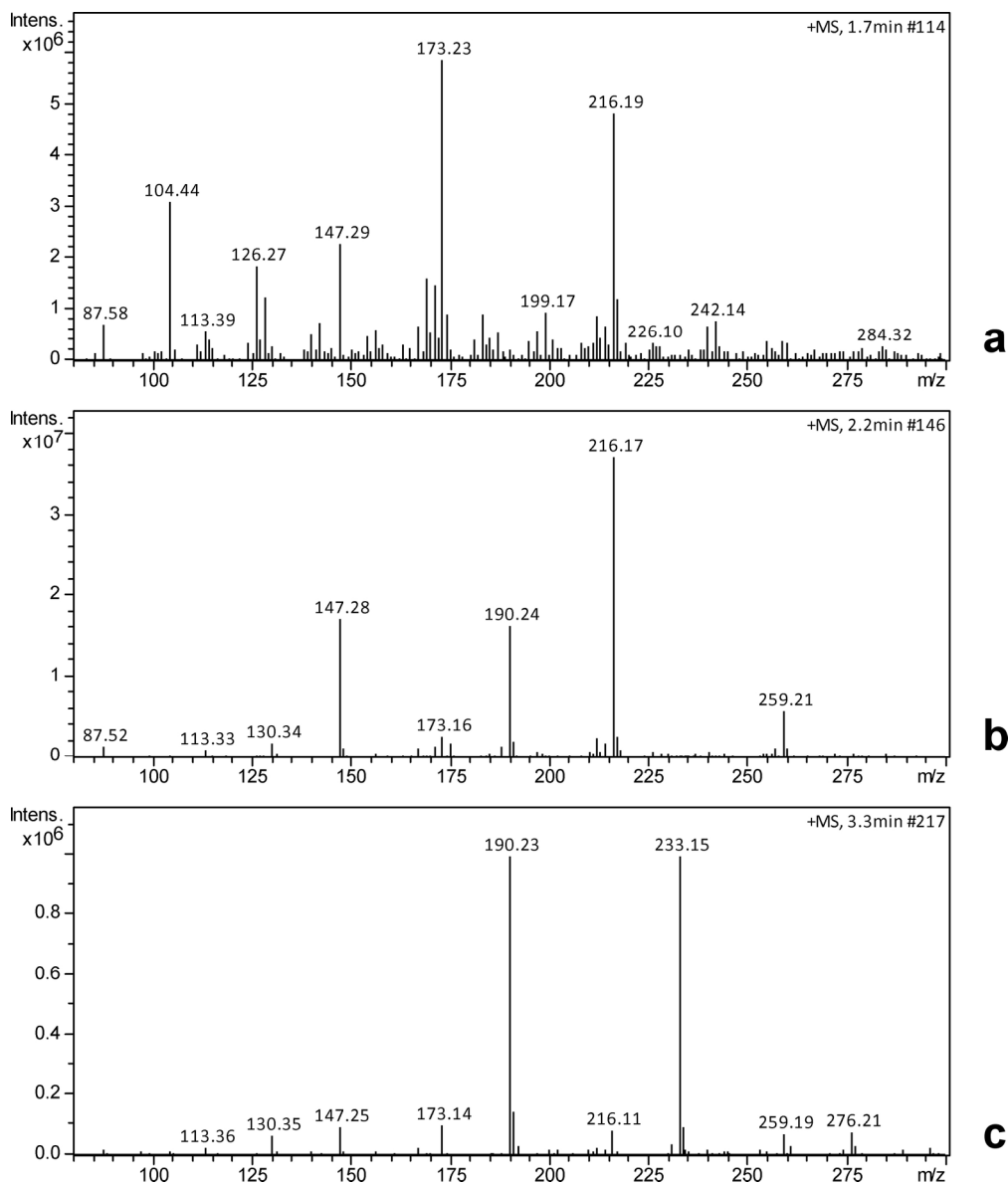


Fig. 8 FAPA-MS spectra of diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenhexamine thermally desorbed from Fe₃O₄-R-COOH after: 1.7 (a); 2.2 (b), and 3.3 (c) minutes from the beginning of the experiment.
97x114mm (600 x 600 DPI)

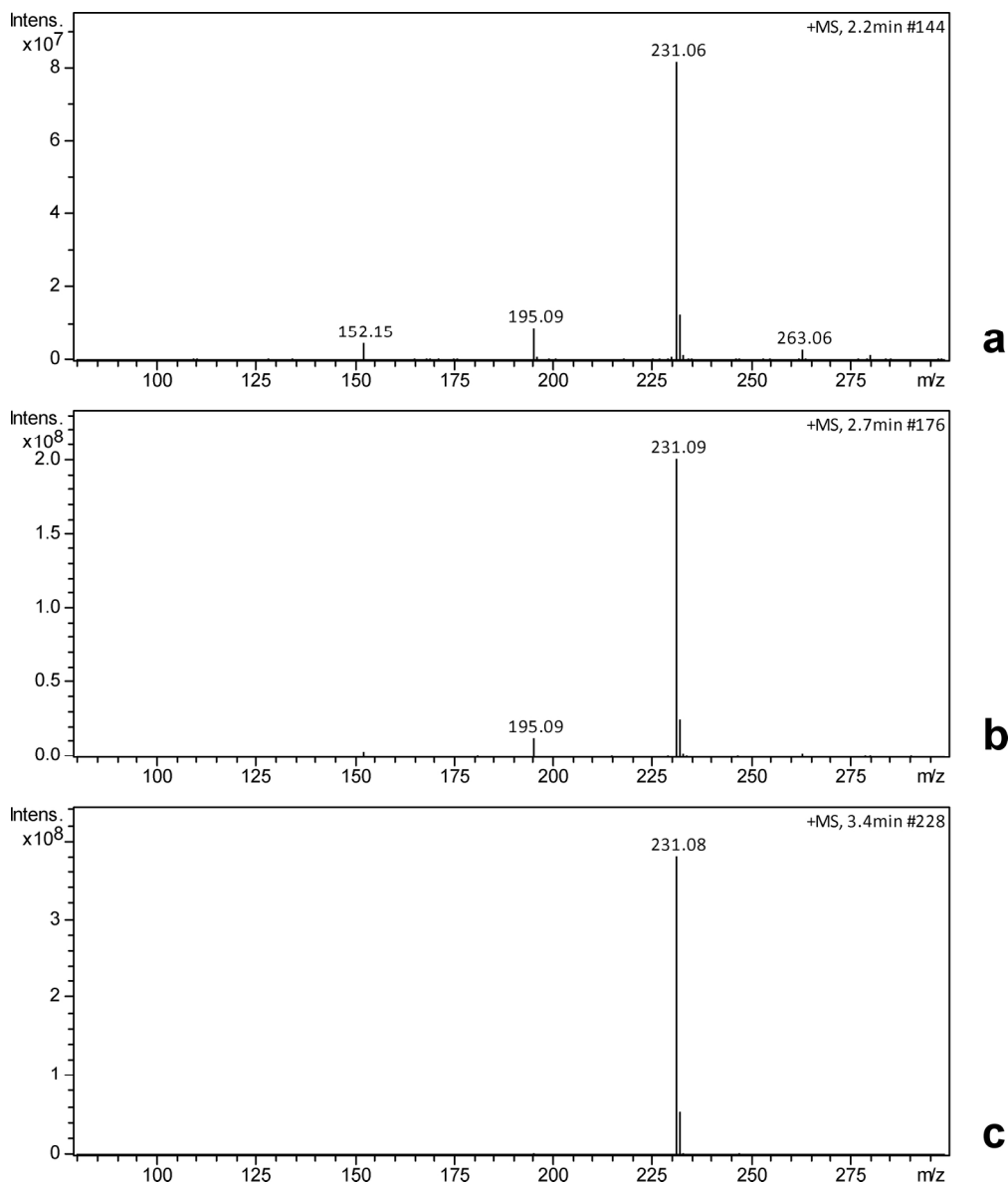


Fig. 9 FAPA-MS spectra of the components of the analgesic drug (paracetamol, caffeine, and propyphenazone), thermally desorbed from Fe₃O₄_R_COOH after: 2.2 (a); 2.7 (b), and 3.4 (c) minutes from the beginning of the experiment.
97x114mm (600 x 600 DPI)

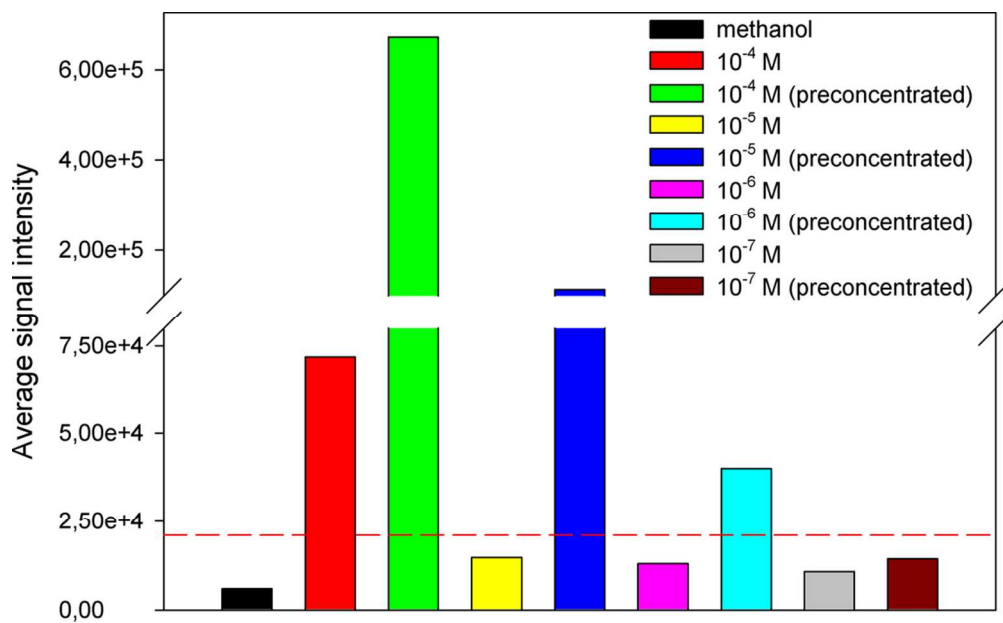


Fig. 10 Limit of detection (LOD); the LOD value (represented by the red dashed line) was calculated as an average signal intensity for reagent blank (methanol) plus three times standard deviation of the reagent blank's signal.
48x29mm (600 x 600 DPI)

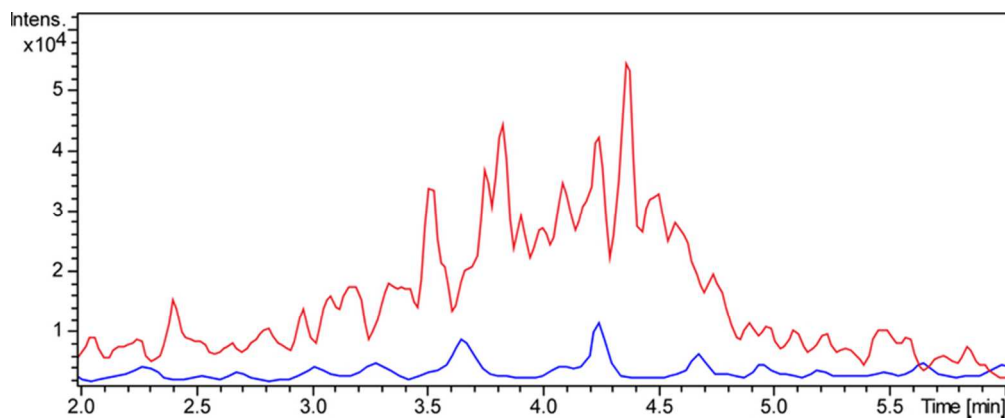


Fig. 11 Extracted ion chromatograms of the signal at m/z 121 obtained for pure methanol (blue line) and for the developed pre-concentration procedure for 10^{-6} M of benzoic acid (red line).
33x13mm (600 x 600 DPI)