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Development and validation of portable membrane inlet mass spectrometry method for measurements of monoaromatic hydrocarbons from the river canal

Brankica Kartalović*, Djordje Vukić, Daria Ilić, Boris Brkić*

This work reports validation of analytical method for determination of monoaromatic hydrocarbons, such as benzene, toluene, and xylene (BTX) using portable membrane inlet mass spectrometer (MIMS) with a quadrupole mass analyser. Our analysis of BTX from the river canal water that is used for irrigation, presents a detailed analytical method for rapid, self-contained, field transportable screening and quantitative analysis for environmental monitoring. The validation study showed that in the analytical range of 10-250 µg/L, the correlation coefficient for all analytes were greater than 0.99, the accuracy was in the range of 95.32-104.30 %, the repeatability precision was less than 10 %, and the satisfactory selectivity of the method was proven. The LOD and LOQ values were ranged respectively for benzene, toluene, and xylene with 4.88, 7.43 and 7.46 µg/L for LOD and 16.27, 24.77 and 27.85 µg/L for LOQ. The method was benchmarked against lab-based GC-MS with accuracy proven for the target compounds.

1. Introduction

In a world increasingly affected by disasters and armed conflicts with power to damage the environment and cause great loss of human life social and economic disruptions, environmental pollution emerged as a global problem. The introduction of harmful substances in all segments of the environment - water, air, and soil, represents a danger for the entire living world. Causality ranges from anticipated natural means (earthquakes, volcanic eruptions, floods) to disasters caused by human means. This, therefore, requires, development of portable instruments that can quickly and reliably, provide information about the pollution in the field and prevent its spreading. The first membrane inlet mass spectrometer (MIMS) was developed in the early 1960’s with main principles described in the work of Kotiaho et al.1,2. A low-impact mass spectrometry technique such as MIMS can be used to identify gaseous and volatile organic compounds (VOC) ranging from solid, liquid to gaseous samples3,4. Since its appearance, MIMS has been widely used for the analysis of soil and water, industrial pollutants including forensics4,5,6. Namely, it has been shown that the portability of the instrument is very important in environmental monitoring. Key aspect of such instruments is in their real-time measurement capability. The review paper of Galuszka et al.7 reports that some official methods from the US Environmental Protection Agency (EPA) are based on portable instruments for determination of pentachlorophenol in soil as well as for determination of 26 elements in soil and sediments with X-ray fluorescence (XRF) spectrometers. Furthermore, an official method for metal determination from air, using a portable instrument is reported in work of Galuszka7 and in the official NIOSH method8. Our study focuses on BTX aromatic hydrocarbons, namely, benzene, toluene, and xylene, which are in a group for the organic water pollutants. BTX can be considered as carriers of pollution from anthropogenic sources as described by Šoštarić9. The last decade of research identified that these compounds can lead to skin irritation, cause irritation of the central nervous system and damage the respiratory organs, while long-term exposure to these entities can be the cause of diseases and illnesses such as cancer organ diseases, etc., as stated by Faiemivo10. Given the fact that BTEX (benzene, toluene, ethylbenzene, xylene) is found in low concentrations in water, as well as the fact that they have low limit values according to current regulations, it has been necessary to developed sensitive and reliable methods for their detection. If we look at different standardized methods, we can see that most of them require pre-concentration of samples, i.e. analytes of interest. Many methods for BTEX detection use gas chromatography (GC) coupled with multiple techniques such as, purge and trap11-14, static headspace (HS)11,14-16, and headspace solid-phase microextraction11,14-16. Liquid-liquid extraction technique is often used as extraction which is time consuming and requires large quantities of solvent (EPA method 551.1)17. Many of these techniques show disadvantages if we look at preparation time, solvent consumption, etc. For example, with the headspace technique, the use of solvents is not required. Furthermore, mostly native samples were used for the analysis. Because of
injection of large amounts of gas into the column, formation of broad peaks problems may occur. To avoid this, it is necessary to reduce or eliminate the use of solvents for sample preparation, as well as to protect the environment and the operator from exposure to toxic organic solvents. For these reasons, methods are developed that require little or no solvents, namely solid phase microextraction (SPME), liquid phase microextraction (LPME) and direct aqueous injection (DAI)\textsuperscript{18,19,21}. These methods are important alternative to the traditional sample preparation methods. They eliminate the disadvantages of conventional extraction methods, such as operation time, large amount of solvent extraction, and the use of specialized apparatus. This was the main reason to develop the solid phase microextraction (SPME) method. SPME enables preconcentration of the analytes from the gas phase into a fibre before the injection into GC/ECD or MS. This method is simple, reliable and achieves the desired level of sensitivity (ng/L), for the analysis of environmental samples\textsuperscript{21}. In addition to the gas chromatography technique for the detection of BTX in water, the liquid chromatography technique is also used with reliable results.

AhSalka et al.\textsuperscript{18} developed and optimised method for high performance liquid chromatography equipped with a photo diode array detector (HPLC-DAD), for simple, reliable determination of BTEX without using high-cost special techniques or large volume of solvents. Wittkamp and Tilotta\textsuperscript{22} describe method of extraction BTEX from the water solution into a solid phase before direct detection by Raman spectroscopy. This serves as example of liquid phase microextraction (LPME) based on the solidification of floating organic microdrops followed by gas chromatography (detection by flame ionization) for preconcentration and determination of benzene, toluene, ethylbenzene, and xylene (BTEX) in water samples\textsuperscript{22}. Common to all listed techniques and methods is the requirement of preparation of samples and analysis in the laboratory, which is not the case with portable instruments and on-site analysis. This important advantage of MIMS in relation to GC-MS is emphasised. Allard and Lauritsen\textsuperscript{21}, presented MIMS as an analytical tool capable of analysing a range of compounds in water without sample preparation and monitoring chemical processes in real time, unlike the traditional VOC analysis using gas chromatography (GC) followed by electron capture detection (ECD) or mass spectrometry (MS) or other noted techniques.

Therefore, over the years, MIMS has gained increasing importance due to its advantages over stationary chromatography\textsuperscript{9}, and the possibility of detecting compounds of interest in the field, right at the scene of an accident. Number of works\textsuperscript{24-27,29,30} on MIMS have shown its suitability for rapid detection in environmental monitoring. Development of portable instruments is important for environmental protection\textsuperscript{24-26}. Furthermore, in-field use of portable analytical equipment provides required intelligence from the scene of the incident\textsuperscript{24-27}, as well as rapid, high detailed results that are crucial for preventing major environmental disasters. The improvement of portable instruments led to the enhancement of quantitative analysis in the field, as shown by Duff\textsuperscript{27}, Fiorentina\textsuperscript{28} and Brkić\textsuperscript{29} at al. Monitoring of the environment was subject of study with notable works in development of portable instruments for rapid analysis of air, water and soil. For example, Brenwald et al.\textsuperscript{30} developed portable mass spectrometric system for continuous on-site analysis of dissolved gases in groundwater such as He, Ar, Kr, N\textsubscript{2} and O\textsubscript{2}. It is important to highlight that those systems do not require any purification or other preparation of the sampled gases and, therefore, allow maintenance-free and autonomous operation. When it comes to environmental monitoring, the importance of rapid identification of VOCs in water with fast response times and high sensitivity has been described by Wu et al.\textsuperscript{32}. They developed helical membrane inlet for time-of-flight mass spectrometry (TOF-MS), which was used for analytes in complex matrix. On the other hand, Brkić et al.\textsuperscript{29} developed portable MIMS system for lab-based water quality monitoring of organic compounds, present in highly toxic nuclear waste ponds. To enhance operation of the MIMS instrument, Armaković et al.\textsuperscript{32} has performed a computational study to assess the possibility of applying polydimethylsiloxane (PDMS) and its structurally similar derivatives (PDMS-HDT and PDMS-TMT) for identification of target naphthenic acids using a portable mass spectrometer.

This paper reports a validation study of a portable MIMS system for in-field analysis of BTX in river canal water. Our MIMS system consists of a quadrupole mass spectrometer with an open ion source, connected to a sample probe with a sheet PDMS membrane inlet as described by Aleksić et. al\textsuperscript{33}. Our laboratory tests were performed on deionized water (DI) enriched with a known concentration of analytes of interest and real water samples taken from the Danube-Tisa-Danube (DTD) canal, known as Hydro-system DTD with (Google, n.d.) coordinates Latitude / Longitude: 44° 57' 22.0314" N / 21° 16' 20.5314" E\textsuperscript{14}. Selected-ion monitoring (SIM) was performed for the target compounds to determine linearity, precision, and accuracy.

We have achieved satisfactory limits of detection (LOD) and limits of quantification (LOQ) as shown in the Results and discussion section.

2. Experimental section

2.1 Concept

The details for the compounds of interest are presented in Table 1, with their molecular weights, target ions and maximum residue levels (MRLs) allowed in drinking and irrigation water. The MRL limits are expressed in micrograms per liter of water (µg/L) as determined by the regulations of the Republic of Serbia\textsuperscript{35,36}, where class I and II can be used for irrigation.
Our testing, calibration, and validation of the MIMS portable analytical system for water quality monitoring was carried out in accordance with the relevant guidance documents. Following the guide points for the validation and verification of quantitative and qualitative test methods and the analytical quality control requirements, we clearly demonstrate that BTX from water can be successfully quantified with a high level of confidence in the results.

### 2.2. Chemicals and supplies

All the chemicals used in the experiments are of analytical grade purity. Anhydrous sodium sulphate powder, HPLC grade methane, and HPLC grade hexane were obtained from Sigma-Aldrich, Australia. The analytical standards for the BTX mix were obtained from Dr. Ehrenstorfer GmbH, Denmark.

The analytical standards of BTX contained three volatile organic compounds that are commonly tested for operational environmental laboratories using GC-MS. Water matrices were used during the method development. The DI water used as a blank did not contain organic contaminants. Smooth standard solution of BTX was prepared in methanol. The working standard solutions with concentrations ranged from 10 to 250 µg/L were prepared step-by-step by dilution with DI water.

For quality control DI water was used as well as water samples from the Danube-Tisza-Danube canal. Real canal water samples were used to test the application of the developed method.

### 2.3 Experimental setup

The experimental setup section describes in depth the MIMS and GC-MS instruments that were used. Sample analysis and the validation plan are also described in detail. The setup of the MIMS system is illustrated in the schematic diagram of Figure 1.

#### 2.3.1 MIMS

The principle of portable MIMS with membrane is based on the pervaporation separation, with a thin polymer-based membrane acting as a barrier between the water and the mass spectrometer. This barrier blocks water and allows only organic compounds to pass through the membrane into the vacuum system. Upon separation, the analytes first enter the ion source for ionization and then the mass analyser for spectral analysis.

Finally, the obtained mass spectra allow the concentration to be determined for the desired analyte in the water sample, based on the intensity of spectral peaks.

All water analyses that were necessary for the validation study were performed using our proprietary portable MIMS instrument. The system comprises of a membrane sample inlet, vacuum chamber, quadrupole mass spectrometer (QMS) with an open electron impact (EI) ion source with yttriated iridium filaments, a 100 mm long single quadrupole mass analyzer (Pfeiffer QMG 250 M3) and a dual detector (Faraday cup and secondary electron multiplier) with a mass range from 1-300 amu. The ECU enables efficient operation specifically designed for partial pressure analysis below 5x10⁻⁶ mbar.

The MIMS system delivers unit resolution, rapid response times (≤0.5 s), and precise measurements at low concentration levels (parts per billion) throughout the entire working mass range as explained by Illi et al. The QMS is mounted inside the vacuum chamber with the ECU close coupled to the QMS flange as described by Brkić et al. The vacuum system consists of a diaphragm pump (MVP 030-3DC) and a turbomolecular pump (HiPace80) purchased from Pfeiffer Vacuum GmbH (Asslar, Germany). It provides the base pressure of 3 x 10⁻⁶ torr which is being monitored by a digital cold cathode pressure gauge (model: MPT 200) supplied by Pfeiffer Vacuum GmbH. MIMS system weighs 25 kg. Dimensions (height x width x length) are 25 x 50 x 60 cm respectively.

A membrane for the inlet is made of polydimethylsiloxane (PDMS). The membrane is 6.5 mm in diameter with a thickness of 120 microns. The membrane probe assembly consists of 10 cm stainless steel tubing coupled with a membrane sheet supported by the 6.35 mm Swagelok stainless steel vacuum fitting union. The non-sterile PDMS membrane sheeting was provided by Technical Products, Inc. of Georgia, USA. The PDMS membrane sheet thickness was 0.12 mm whereas the sampling area was 33.2 mm². The membrane was supported by a 0.8 mm thick stainless steel porous frit with 20 µm porosity.
written in R language for automated determination of analyte concentrations. Analyte identification was done by observing characteristic ions that did not have overlaps with mass fragments from other compounds. Calibration curves were created based on the intensity of the observed ion. Using MIMS, water was analysed in the field in near real-time.

2.3.2 Laboratory-based GC–MS
For the validation study of the MIMS, all the results were compared to those obtained by an Agilent GC-MS headspace 7890A/7694E (Hewlett Packard Technologies, USA). The instrument used a 30-m Agilent J&W DB-5MS Ultra Inert column (0.25 mm × 0.25 µm film thickness). The column temperature started at 40 °C for 3 minutes and increased by 20 °C per minute until it reached 150 °C where it was kept for an additional 1.5 min, giving a runtime of 10 min. Injection volume was 2 mL, and headspace syringe temperature was 105 °C. The MS parameters were set at the following values: electron impact ionization with 70 eV energy; transfer line temperature at 280 °C; ion source temperature at 230°C and QMS temperature at 150 °C. BTX ions chosen for quantification were m/z 77, 78 for benzene, m/z 91, 92 for toluene, m/z 105, 106 for xylene. 

GC-MS headspace calibration was done with Aromatic Mix, purchased from Sigma-Aldrich, St. Louis, MO, USA. A series of solutions in the range of 10-250 µg/mL was made using DI water in a total volume of 5 ml.

2.4 Sample analysis
The developed method for water analysis was based on the method that was first demonstrated for oil-in-water monitoring by Brkić et al. During the field tests for the river canal water, the membrane sample probe was connected to the water flow system via 1/4 in. flexible PA hose. The field method was evaluated against the laboratory method for the quantitative analysis of target compounds. The assessment was based on the validation study for testing residues of benzene, toluene and xylene in water using two instruments and two different techniques. DI water and water from the DTD canal were used for the validation study. Laboratory verification was performed with DI water spiked with a known concentration of the analyte of interest using BTX liquid reference standards. Appropriate volumes of each liquid stock solution were injected with high-precision micropipettes (Dr. Ehrenstorfer, Denmark) into a glass aquarium in amounts that provide concentrations of 10, 25, 50, 100 and 250 µg/L for each analyte of interest. The aquarium was filled with water to provide a total volume of 20 L. It was covered with a lid with temperature-controlled water at 25 °C to achieve thermodynamic equilibrium and stable conditions. To ensure the homogeneity of the sample, pumps were used to constantly mix the contents of the aquarium. Before starting the analysis, all the glassware was carefully washed to remove all interference with other volatile compounds. Reference standards were tested from lowest concentration to highest. This was done to reduce cross-contamination. During tests, membrane probe was directly inserted into the aquarium, and it was used for sampling of the prepared water with known standards for concentrations. The membrane probe and subsequently the membrane were kept at ambient temperature throughout the measurements. The sample was introduced directly into the vacuum system.

2.5 Validation plan
The aim of the validation plan was to confirm that the method developed using MIMS can be used in the field with high level of confidence for the quantitative real-time analysis of BTX from the canal water. Validation plans included definition of the analytical range, confirmation of the selectivity of the method, linearity verification (R² > 0.99) as well as precision (<10%), recovery (80-110%), determining the limit of detection (LOD) and limit of quantification (LOQ).

To investigate linearity of the MIMS, we used five-point calibration. For laboratory tests, we used standard reference materials and DI water. Real water samples from the canal and DI water with and without the addition of a known analyte concentration, were used for quality control and verification of the accuracy of the method. Measurement was done in the same condition four times at two levels, to determine the precision of the instrument as well as to determine the limit of detection and quantification. The accuracy check was done with water from the DTD canal, with added known concentration of the analyte, to consider the influence of the matrix on the result. In this study, LOQ represents the lowest concentration that can be determined with acceptable accuracy, while LOD is the lowest concentration that can be proven, but not determined with appropriate accuracy.

3. Results and discussion
3.1 BTX experimental plan
The analysis of BTX in water and the total time of the on-site analysis was ~10 minutes, similar to the work by Hu et al. On the other hand, Duff et al. used SPME fibres with a portable MIMS to achieve rapid on-site analysis. They reported analysis time of 6.5 minutes. During the validation study, all the tests were performed in the analytical range from 10 to 250 µg/L to confirm linearity, specificity and selectivity, accuracy, precision of the method, and detection and quantification limits.

3.2 Method linearity
In the reported analytical range from 10 to 250 µg/L, linearity was assessed using five calibration points with satisfactory correlation factor R²>0.99 for all the compounds of interest. Given the fact that the range of linearity depends on the nature of the analyte, the influence of the matrix, the type of detector and the type of portable instrument, different authors reported different correlation factors for their research.

Thus, Brkić et. al reported correlation factors > 0.98 for group of alcohols, ketones and aldehydes detected in nuclear waste lakes, while Wu et al. reported a correlation factor for benzene > 0.99 and for xylene > 0.98. Figure 2 shows the intensity of characteristic ions and calibration curves for benzene, toluene, and xylene in water using portable MIMS. The results were obtained under controlled laboratory conditions.
We have conducted four replicate tests on three analytes in water, using the optimized procedures to assess the precision of the new method. The precision results are presented in Table 2. Based on the table, it is evident that the presented approach achieves sufficient precision to fulfill the requirements for BTX analysis in water using portable MIMS. This is because the relative standard deviation (RSD) of this method is below 2.60%, indicating high precision of the proposed method.

Table 2. Method repeatability precision

<table>
<thead>
<tr>
<th>Replica No.</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>105.2</td>
<td>97.1</td>
<td>98.1</td>
</tr>
<tr>
<td>2</td>
<td>106.1</td>
<td>96.7</td>
<td>102.8</td>
</tr>
<tr>
<td>3</td>
<td>102.6</td>
<td>95.8</td>
<td>99.3</td>
</tr>
<tr>
<td>4</td>
<td>103.3</td>
<td>91.7</td>
<td>97.1</td>
</tr>
<tr>
<td>RSD, %</td>
<td>1.56</td>
<td>2.60</td>
<td>2.50</td>
</tr>
</tbody>
</table>

To confirm the accuracy of the method, we compared the measurement results of an enriched sample of the canal water obtained using portable MIMS and benchtop GC-MS. Table 3 shows the measured BTX values from the enriched water samples. It is evident that the relative differences (RD) between these techniques were within 4.89%, which indicates the accuracy and reliability of the observed portable MIMS method for the quantitative analysis of BTX from water.

Table 3. Method comparison

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>MIMS method</th>
<th>GC-MS method</th>
<th>Relative difference, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>105.2</td>
<td>100.3</td>
<td>4.89</td>
</tr>
<tr>
<td>2</td>
<td>106.1</td>
<td>101.2</td>
<td>4.84</td>
</tr>
<tr>
<td>3</td>
<td>102.6</td>
<td>100.6</td>
<td>1.99</td>
</tr>
<tr>
<td>4</td>
<td>103.3</td>
<td>100.1</td>
<td>3.2</td>
</tr>
<tr>
<td>STD</td>
<td>0.32</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>97.1</td>
<td>100.2</td>
<td>-3.09</td>
</tr>
<tr>
<td>2</td>
<td>96.7</td>
<td>98.5</td>
<td>-1.83</td>
</tr>
<tr>
<td>3</td>
<td>95.8</td>
<td>99.3</td>
<td>-3.52</td>
</tr>
<tr>
<td>4</td>
<td>91.7</td>
<td>95.9</td>
<td>-4.38</td>
</tr>
<tr>
<td>STD</td>
<td>2.48</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>98.10</td>
<td>100.20</td>
<td>-2.1</td>
</tr>
<tr>
<td>2</td>
<td>102.80</td>
<td>101.30</td>
<td>1.48</td>
</tr>
<tr>
<td>3</td>
<td>99.30</td>
<td>99.81</td>
<td>-0.5</td>
</tr>
<tr>
<td>4</td>
<td>97.10</td>
<td>102.20</td>
<td>-4.99</td>
</tr>
<tr>
<td>STD</td>
<td>2.40</td>
<td>1.09</td>
<td></td>
</tr>
</tbody>
</table>

Our validation study requires verification recovery value that will represent the accuracy of the analytical method as a degree of agreement between the actual value and the value obtained by applying the analytical procedure with certain number of times. This indicates the fidelity of the measurement. Depending on the substances and the matrix effect, some
authors have reported recoveries ranging from 50.0 to 87.5%, for example the study of Fiorentin et al.\textsuperscript{28} Our results gave 95.32% for toluene, 99.32% for xylene and 104.30% for benzene. To determine the accuracy of the field analysis, the results obtained with the portable MIMS were compared to those obtained on a benchtop GC-MS, using a same range of BTX that can be identified by both methods. Native samples were used in both techniques. Although these compounds were present in lower concentrations, they could still be observed in both instruments. All major peaks detected using the field-based method were also detected using benchtop GC-MS for all the materials burned. Figure 4a shows a representative benchtop GC-MS chromatogram. The peaks of interest were also detected in the field using the portable MIMS as shown in Figure 4b.

![Image](https://example.com/figure4.png)

**Figure 4.** Representative benchtop gas chromatography-mass spectrometry (GC-MS) chromatogram (a) compared to a portable MIMS mass spectrum (b) for the canal water sample.

### 3.5 Method Limit of Detection and Limit of Quantification

The results for LOQ and LOD values from MIMS are shown in Table 4.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>MIMS (LOD), µg/L</th>
<th>MIMS (LOQ), µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4.88</td>
<td>16.27</td>
</tr>
<tr>
<td>Toluene</td>
<td>7.43</td>
<td>24.77</td>
</tr>
<tr>
<td>Xylene</td>
<td>7.46</td>
<td>24.85</td>
</tr>
</tbody>
</table>

To provide an estimate of the LOQ and LOD values for the target compounds, an analytical standard of 10 mg/L was used, which was added to the water sample at a defined concentration range. After performing ten-times measurement of the first point of calibration, LOD and LOQ were calculated. Our results show that the LOQ values obtained by validation are significantly lower than the MRL values for irrigation water and slightly above the MRL values for drinking water, observing the regulations of the Republic of Serbia. If we compare the LOD values of different authors, we can see that the LOD value depends not only on the matrix and the type of compound, but also on the instrument itself.

In the work of Wu et al.\textsuperscript{31}, who used a helical membrane inlet single photon ionization time-of-flight mass spectrometry (SPI-TOFMS), the reported LOQ values for benzene and xylene were respectively 0.014 and 0.036 µg/L. These are significantly less than the LOQ values obtained in our study. Fiorentin et al.\textsuperscript{28} reported that detection limits were in the range of 0.01 to 0.1 mg/mL for some drugs (higher molecular weight than BTX). Hu et al.\textsuperscript{42} reported limits of detection in the low parts-per-trillion levels (≤5.25 ng/L) for the determination of persistent organic pollutants (polychlorinated biphenyls, organochlorine pesticides and polycyclic aromatic hydrocarbons in total analysis time only of 30 min.

It is, therefore, important to emphasize that the use of portable instrumentation is not intended to replace laboratory analysis, but rather to obtain an in-field alert report of the polluted site to take actions to protect the environment. This will require immediate quantitative validated results. In such situations, the concentrations of pollutants are generally high, in contrast to environmental monitoring, where the concentrations of pollutants are at residual, expected levels.

### 4. Conclusions and Future Work

In this study, we used a portable MIMS instrument to develop and validate a method for rapid quantitative analysis of BTX in the river canal irrigation water within a defined analytical range. The results confirmed linearity, precision, selectivity, measurement and accuracy of the method. Future work will involve pilot tests in the DTD hydro canal with the aim of collecting data on the loading of irrigation water with monoaromatic hydrocarbons and improving the quality of the environment. Real-time quantitative analysis will also be performed not only for BTX, but also for other dissolved hydrocarbons of interest. Considering the results obtained for LOQ and LOD (µg/L level), in the following period, work will be done on improving the sensitivity of our proprietary portable MIMS device with an effort to be used for drinking water monitoring as well as in rapid screenings of drinking water in accidental situations.

### Author Contributions

B.K. - Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Writing – review and editing. D.I. - Formal analysis, Visualization. Dj.V. – Methodology, Visualization. B. B. – Supervision, Conceptualization, Methodology, Writing – original draft, Writing – review and editing.

### Conflicts of interest

There are no conflicts to declare.

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A Data Availability Statement

Data for this article, including original data for figure creating are available at University of Novi Sad at https://open.uns.ac.rs/handle/123456789/32772