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DEVELOPMENT AND APPLICATION OF AN OPTIMIZED TD-GC/MS METHOD FOR MONITORING VOLATILE ORGANIC COMPOUNDS (VOCs) IN AMBIENT AIR

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Abstract

Volatile Organic Compounds (VOCs) are organic chemicals with high vapor pressure, originating from natural and anthropogenic sources, and are major contributors to environmental issues like photochemical smog and atmospheric pollution. This study introduces an optimized TD-GC-MS method for detecting and quantifying VOCs in ambient air, employing internal standards and certified reference materials to ensure analytical accuracy and traceability. The method is designed to deliver exceptional sensitivity, precision, and reproducibility, suitable for diverse environmental conditions. Key improvements include optimized thermal desorption, fine-tuned chromatographic separation, and calibrated mass spectrometric detection. Aligned with Eurachem guidelines, the integration of internal standards mitigates instrumental variability, while certified reference materials ensure traceable calibration, enhancing result reliability. The research demonstrates the method`s applicability to air quality monitoring, environmental assessments, and public health research. The findings validate TD-GC-MS as a robust, reliable solution for continuous VOC monitoring and routine environmental applications, providing critical insights into pollution sources and impacts, particularly in urban and industrial contexts. This research addresses the needs of scientists, policymakers, and environmental professionals seeking effective tools to combat air pollution.

Key words*: air quality monitoring, environmental pollution, GC-MS, thermal desorption, Volatile Organic Compounds.*

INTRODUCTION

Volatile Organic Compounds (VOCs) are produced from both natural and anthropogenic sources (Piccot et al., 1992). Natural sources include microbial activity, marine phytoplankton, volcanic and geothermal emissions, as well as wildfires (Ling & Guo, 2014). Anthropogenic sources comprise petroleum extraction and refining, vehicle emissions, the production and application of solvents on different surfaces, incomplete combustion of fossil fuels or biomass, and the fugitive emissions of VOCs from plastic materials during regular use (Atkinson & Arey, 2003). In the atmosphere, non-methane volatile organic compounds (VOCs) react with nitrogen oxides (NOx) in the presence of UV radiation, leading to the formation of ground-level ozone (O_3), a key component of photochemical smog. This reaction significantly contributes to air pollution and has detrimental effects on human health, both aquatic and terrestrial ecosystems, and plays a crucial role in climate change (Li et al., 2018). Elevated ground-level ozone concentrations can deteriorate air quality and lead to severe health problems, including respiratory conditions, heart disease, and cancer (Alford & Kumar, 2021). Prolonged exposure to VOCs has also been linked to neurological disorders, liver and kidney damage, and developmental issues, particularly in vulnerable groups like children and the elderly (Agency for Toxic Substances and Disease Registry, 2007).
The health impacts of VOC exposure depend on the specific compound, its concentration, and the duration of exposure. Brief exposure to high levels of VOCs, including benzene, toluene, and formaldehyde, can cause symptoms like irritation of the eyes and throat, headaches, dizziness, and nausea (Alford & Kumar, 2021). Long-term exposure, especially in urban and industrial zones, is associated with more severe health consequences, such as diminished lung function, weakened immune response, and reproductive issues. Some studies suggest a link between chronic VOC exposure and neurodegenerative diseases, underscoring the

need for stricter air quality regulations (Mølhave, 1991; Li et al., 2018).

In this regard, accurate monitoring of VOCs is essential for pollution control, regulatory compliance, and public health studies. In Romania, VOCs in ambient air are regulated by Law 104/2011 regarding air quality, which establishes a threshold value for the hazardous compound benzene, while other compounds such as toluene, ethylbenzene, and xylene (BTEX) are subject to general European regulations. According to the same law, benzene, in particular, is required to be monitored in major urban areas, given its significant concentration from human activities like traffic and industrial operations (Law No. 104, 2011). Other VOCs of concern include dichloroethene, dibromochloromethane, carbon tetrachloride trichloroethene, ethylbenzene, chlorobenzene, styrene, naphthalene et. all. These compounds contribute to atmospheric pollution and must be carefully monitored to assess their environmental impact and ensure regulatory compliance (Maceira et al., 2017).

Nowadays, several methods are available to detect VOCs in ambient air, including portable sensors such as the Photoionization Detector (PID) and Flame Ionization Detector (FID), as well as analysers utilizing Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet (UV) fluorescence (Qualley et al., 2019; Epping & Koch, 2023; Elia et al., 2024). Each method has different advantages, such as real-time monitoring, simultaneous measurement of multiple compounds, and not requiring complex sample preparation. However, they also have disadvantages, such as poor selectivity, sensitivity and reduced precision. On the other hand, Thermal Desorption Gas Chromatography coupled with Mass Spectrometry (TD-GC-MS) offers increased selectivity (in multiple reaction monitoring mode) and specificity (Jia et al., 2006). Additionally, the method is quite robust, reproducible, and traceable, which facilitates compliance with regulatory standards and enhances our understanding of air pollution dynamics. Moreover, it is crucial to monitor non-methane VOCs (NMVOCs) as defined in Law No. 104/2011, including aliphatic hydrocarbons (such as ethane, propane, and butane), aromatic hydrocarbons (such as benzene, toluene, and xylene), oxygenated compounds (such as ethanol and acetone), and halogenated compounds (such as CFCs and halons). These VOCs contribute significantly to the formation of tropospheric ozone, a harmful pollutant that can adversely affect human health, especially in regions with high levels of emissions (Zhou et al., 2023).

MATERIALS AND METHODS

The analysis of VOCs in ambient air using Gas Chromatography-Mass Spectrometry (GC-MS) requires calibration across multiple concentration levels, achieved through serial dilution of certified standard solutions. (Rodríguez-Navas et al., 2012; Cai et al., 2015; Chung et al., 2019). Thus, the following reference mixtures were used for calibration:

502.2 Calibration mix 30043, Batch A0189182;
502.2 Calibration mix 30044, Batch A0180278;
502.2 Calibration mix 30045, Batch A0181037;
502.2 Calibration mix 30046, Batch A0175597;
502.2 Calibration mix 30047, Batch A0189197.

The reference mixtures, manufactured by RESTEK, were diluted with Methanol SupraSolv 1.00837.1000, using Eppendorf Xplorer plus micropipettes 0.5-10 µL and Eppendorf Xplorer plus 0.2-5 mL pipettes.

TD glass tubes filled with deactivated glass wool (Restek, Deactivated wool 24324, Batch 365237-1) were used for the introduction of substances, and the calibration solutions were introduced by dispensing 1 µL of each solution using a Shimadzu 10 µL syringe (10F-S-0.63, Batch 51W-074109M).

Analytical analysis of Thermal Desorption (TD) Tubes was performed using the Shimadzu Thermal Desorption System TD 30R, with a temperature program of 10 minutes at 280°C and 70 ml/min, followed by trap cooling to -20°C (Brown & Crump, 1998). The analyses were carried out using the Shimadzu Gas Chromatograph Mass Spectrometer - TQ8050NX, coupled with an SH-5Sil MS chromatographic column for effective separation of VOCs. The mass spectrometer was operated in both SCAN mode, where a broad range from 50 m/z to 350 m/z was rapidly scanned to capture a full spectrum of ions in order to identify the retention time for each VOC compound, and Selected Ion Monitoring (SIM) mode, where the mass spectrometer focused on

specific ions of VOC compounds within this range to enhance sensitivity and selectively detect VOC compounds (Pleil et al., 1991). The gas chromatograph temperature program for VOCs separation is presented in Figure 1.

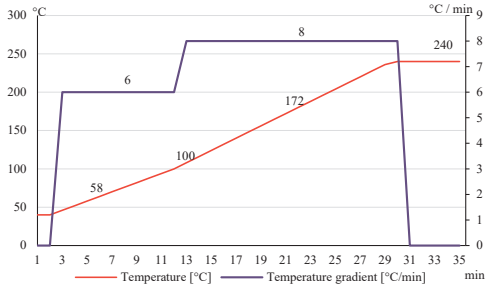

Figure 1. GC temperature profile for VOCs separation

Sampling of VOCs in ambient air was performed on TD tubes, Tenax 60/80 mesh, O.D x L ¼ in x 3 ½ in glass and Tenax TA/Carboxen1018, O.D x L ¼ in x 3 ½ in glass from Markes International (Figure 2), using the Acti-VOC Low Pump from Markes International (SN: 20220201001). The pump flow rate was calibrated for the desorption tubes using the 7000 Flowmeter from Ellutia (SN: 200235).

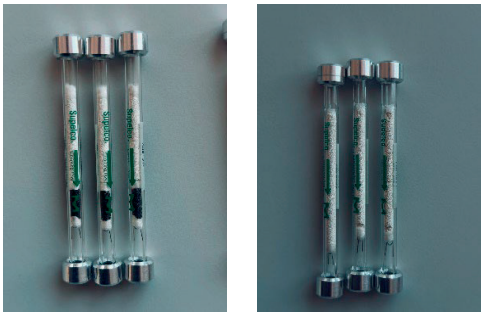

Figure 2. Tenax TA/Carboxen1018 and Tenax TA tubes

Additionally, helium 6.0 was used as the carrier gas, deuterated toluene as the internal standard from Linde Gaz Romania, also 4 mL glass vials and racks from Shimadzu were employed for sample storage.

RESULTS AND DISCUSSIONS

The optimalization of the chromatographic method was conducted to ensure its robustness, precision, and reliability. In this context, key performance parameters were evaluated according to established international standards (Eurachem/CITAC Guide; 2012; Eurachem, 2025; SR EN ISO 17025, 2018), along with the analytical conditions of the mass spectrometer used for detection. Linearity was assessed by evaluating the correlation coefficient (R^2), confirming the proportional relationship between analyte concentration and detector response within the defined range. Similarly, the limit of detection (LOD) and limit of quantitation (LOQ) were determined by analyzing the signal-to-noise ratios and the regression line intercept, which reflect the method's sensitivity in detecting and quantifying low analyte concentrations. The precision of the method was assessed by examining intra- and inter-day reproducibility, with the relative standard deviation (RSD) being used to evaluate variability across various concentration levels. Accuracy was confirmed through recovery studies, where theoretical concentrations were compared with measured values. In addition, specificity was evaluated to ensure the method's ability to effectively separate the analyte from potential matrix interferences.

In addition, the analytical conditions of the mass spectrometer, including ionization source parameters, collision energy, and mass resolution, were optimized and validated to ensure accurate and reproducible measurements. These conditions were carefully adjusted to achieve maximum sensitivity and specificity for the target analyte.

Development of solutions at multiple concentration levels

Multiple concentration levels were carried out starting from a stock solution of 2000 µg/mL, using the following calibration mixtures from Method 502.2: Calibration mix 30043 (Batch A0189182), Calibration mix 30044 (Batch A0180278), Calibration mix 30045 (Batch A0181037), Calibration mix 30046 (Batch A0175597), and Calibration mix 30047 (Batch A0189197). These mixtures were dissolved in methanol to create eight concentration levels: 0, 1.6, 3.5, 5, 8, 10, 19, and 32 ng, ensuring a comprehensive calibration range for the analyte. The VOCs (volatile organic compounds) were quantified across these levels to evaluate the

method's effectiveness in detecting and measuring these compounds.

Mass spectrometer tuning and optimization

The United States Environmental Protection Agency (US EPA) methods for VOC analysis in ambient air recommend adjusting the tuning conditions by modifying the perfluorotri-butylamine (PFTBA) target abundances to ensure that subsequent 1-Bromo-4-fluorobenzene (BFB) analysis meets the established relative abundance criteria (U.S. Environmental Protection Agency, 1999; 2003). Thus, the research supports the recommended BFB tune conditions using m/z 69 as the target mass and mass pattern adjustment, as presented in Table 1.

Table 1. 1-Bromo-4-fluorobenzene tuning conditions

Mass (m/z)	Intensity Ratio %
69	100
219	50
502	1.5
131	42
414	2.5
614	0.4

The tuning process was performed on the Shimadzu GCMS-TQ8050NX using an automated tuning procedure prior to sample analysis. The optimized conditions ensure stable instrument performance, enhancing sensitivity and accuracy in VOC quantification (U.S. Environmental Protection Agency, 2025). Regular tuning verification, following United States Environmental Protection Agency (US EPA) protocols, maintains compliance with analytical standards and ensures reproducible results throughout the study.

Studies have shown that these conditions produce a tune that meets the strict BFB relative abundance criteria for all VOC methods across multiple instruments and remains stable over an evaluation period of approximately three months (Shimadzu, 2023). Additionally, the tune file obtained was applied to the Thermal Desorption-Gas-chromatography-Mass spectrometry (TD-GC-MS) method, ensuring optimal ionization efficiency and accurate mass detection for VOC analysis.

The stability of the tuning parameters was maintained throughout the thermal desorption process, ensuring reliable quantification of target compounds.

Selectivity and specificity

The method's selectivity was achieved through the SH-5Sil (0.25 mm x 0.25 µm x 30 m) chromatographic column, renowned for its high efficiency and low bleed characteristics. The column facilitated the precise separation of complex VOC mixtures present in different matrices (ambient air), with distinct retention times (Table 2) for each compound (Figure 3). The effective resolution of individual VOC peaks within the chromatogram was crucial in preventing peak overlap and enhancing the method's sensitivity. This superior selectivity ensured the accurate identification and quantification of each VOC in the challenging environmental matrix.

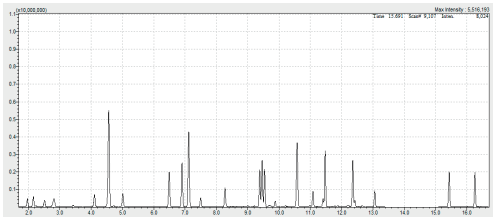

Figure 3. Separation of VOCs in ambient air

To further enhance the specificity and sensitivity of the analysis, the mass spectrometer was operated in Selective Ion Monitoring (SIM) mode. In this configuration, three ions were meticulously selected for each compound: one quantifier ion (e.g., 78 m/z for benzene) and two qualifier ions (e.g., 77 m/z, 51 m/z) to confirm compound identity (Figure 4), following the guidelines established by the TO-14, TO-15, and TO-17 methods for VOC analysis.

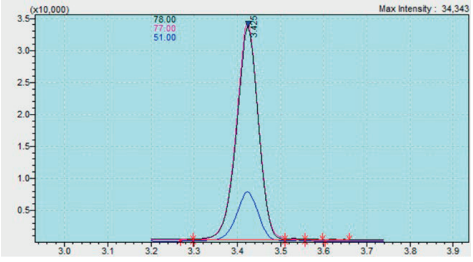

Figure 4. Benzene quantifier and qualifier ions (m/z)

This dual-ion approach ensures the integrity of the analysis by enabling compound-specific verification. The SIM mode provided substantial improvements in sensitivity, reducing background noise and minimizing potential interferences from non-target compounds. Through this integration of selectivity, chromatographic resolution, and ion-specific detection, the method achieved a high degree of specificity and reliability, making it suitable for the precise.

Linearity Assessment and Calibration Curve Validation for VOC Quantification

The linearity of the method was assessed by constructing a calibration curve through the injection of a series of calibration standards onto the thermal desorption tube at distinct concentration levels (0, 1.6, 3.5, 5, 8, 10, 19, and 32 ng), as detailed in the experimental procedure. The ambient air matrix was spiked with precisely known concentrations (theoretical concentrations) of target VOCs, while the internal standard method utilizing deuterated toluene was implemented to ensure robust and accurate quantification. The data obtained were then employed to generate calibration curves for each analyte (Table 2), ensuring that a comprehensive range of concentrations was thoroughly represented.

Table 2. Correlation Coefficient (R), Coefficient of Determination (R^2), and Retention Times for VOC Calibration Curves

Compound name	Retention time (min)	R Coefficient	R^2 Coefficient
Dichloroethene	1.950	0.99961	0.99923
Cis - 1,2 dichlorethene	2.157	0.99982	0.99965
1,1 - Dichloroethane	2.250	0.99817	0.99963
Bromochloromethane	2.500	0.99972	0.99972
Chloroform	2.505	0.99864	0.99973
1,1,1 - Trichloroethane	2.801	0.99987	0.99974
1,2 - Dichloroethane	2.802	0.99992	0.99985
Carbon tetrachloride	3.000	0.99985	0.99969
Benzene	3.434	0.99988	0.99976
Dibromomethane	3.450	0.99976	0.99952
1,2 - Dichloropropane	3.425	0.99983	0.99966
Trichloroethene	3.425	0.99956	0.99912
Bromodichlorometh.	3.587	0.99985	0.99971
cis13-Dichloropropene	4.101	0.99988	0.99975
tra13-dichloropropene	4.602	0.99977	0.99955
Toluene	4.620	0.99980	0.99961
1,1,2 - trichloroethane	4.720	0.99979	0.99957
1,3 – Dichloropropane	5.000	0.99970	0.99985
Dibromochlorometh.	5.250	0.99977	0.99954
1,2-Dibromoethane	5.498	0.99987	0.99975
Tetrachloroethene	5.590	0.99975	0.99950
Chlorobenzene	6.500	0.99982	0.99965
1,1,1,2-Tetrachloroeth.	6.600	0.99981	0.99962
Ethylbenzene	6.980	0.99984	0.99968
mp-Xylene	7.188	0.99978	0.99957
Bromoform	7.500	0.99942	0.99884
Styrene	7.684	0.99987	0.99974
o-Xylene	7.756	0.99936	0.98729
1,1,2,2-Tetrachloroeth.	8.300	0.99929	0.99858
1,2,3Trichloropropane	8.501	0.99980	0.99960
Isopropilbenzene	8.651	0.99982	0.99963
Bromobenzene	8.800	0.99984	0.99968
o-Chlorotoluene	9.382	0.99925	0.99849
n-Propylbenzene	9.491	0.99479	0.98961
4-Chlorotoluene	9.555	0.99978	0.99957
1,3,5-Trimethylbenz.	9.850	0.99982	0.99636
S-butylbenzene	11.101	0.99980	0.99960
1,4-Dichlorobenzene	11.103	0.99978	0.99956
p-Cymene	11.510	0.99968	0.99936
1,2-Dichlorbenzene	11.770	0.99981	0.99961
n-Butylbenzene	12.360	0.99864	0.99728
1,2,4-Trichlorobenz.	15.451	0.99974	0.99948
Naphthalene	15.625	0.99986	0.99973
1,2,3-Trichlorobenz.	16.241	0.99966	0.99932
Hexachlorobutadiene	16.528	0.99968	0.99935

Each calibration point for the VOCs was determined based on the quantifier ion (e.g., 78 m/z for benzene), which was selected to ensure precise and consistent quantification (Figure 5).

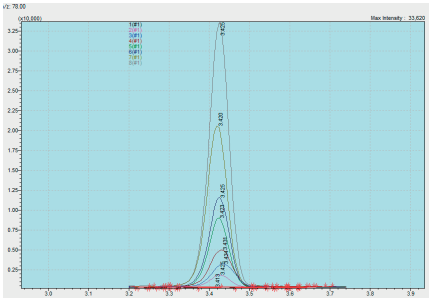

Figure 5. Peak identification quantifier ion 78 m/z

This methodological approach facilitated a comprehensive evaluation of the system's capacity to generate a consistent and linear response across the defined concentration spectrum, which is critical for the accurate and reliable quantification of VOCs in complex environmental matrices. The calibration curves were meticulously constructed by plotting the peak area of each analyte against its corresponding concentration (Figure 6), ensuring a broad concentration range was covered.

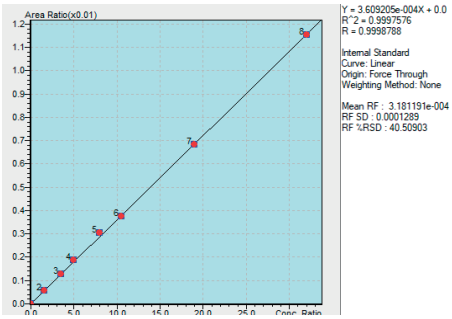

Figure 6. Calibration curve for benzene quantification

Additionally, the internal standard response was strategically employed to correct for potential variations, such as instrumental fluctuations or matrix interferences, thereby ensuring the precision of the quantification process.

The calibration data obtained were used to rigorously evaluate the linearity of the method across the specified concentration range, thereby affirming the precision and robustness of the analytical technique. The calibration curve, along with the comprehensive table displaying the correlation coefficients (R and R^2) for each analyte, was utilized to provide a detailed representation of the method's consistency for quantification of VOCs in ambient air.

Poor correlation coefficients were observed for 1,2-Dibromo-3-Chloropropane, tert-Butylbenzene, 1,2,4-Trimethylbenzene, and 1,3-Dichlorobenzene, and their signal intensities increased significantly, causing interference with the detector. This interference, likely caused by the injection of deuterated toluene (d8), compromised the accuracy and reliability of their quantification. For both technical and economic considerations, these compounds were excluded from the analysis to maintain the integrity and efficiency of the method.

Analytical Performance Parameters: Repeatability, Limit of Detection, Limit of Quantification, and Recovery

Ensuring the reliability and accuracy of an analytical method is essential in environmental monitoring, particularly when using Gas Chromatography-Mass Spectrometry (GC-MS) for the determination of volatile organic compounds (VOCs) in ambient air. The validation process involves assessing key performance parameters that define the method's precision, sensitivity, and accuracy. Among these, repeatability, limit of detection (LOD), limit of quantification (LOQ), and recovery are crucial for determining its suitability for air quality assessment and regulatory compliance (Eurachem, 2025).

Repeatability refers to the method's ability to produce consistent results when the same air sample is analyzed multiple times under identical conditions. It is a key aspect of precision and is expressed as the relative standard deviation (RSD) of repeated measurements. Repeatability is assessed both within the same day (*intra-day precision*) and across multiple days (*inter-day precision*) to ensure robustness. The results of these evaluations are summarized in Table 3, which presents the intra-day and inter-day repeatability data for VOCs in ambient air.

Limit of Detection (LOD) represents the lowest concentration of a VOC that can be detected but not necessarily quantified with confidence (Eurachem, 2025). It is a crucial parameter for evaluating the sensitivity of an analytical method, particularly when analyzing trace-level VOCs in urban and industrial environments. LOD is often determined using statistical approaches based on the signal-to-noise ratio or the standard deviation of the baseline noise.

Limit of Quantification (LOQ) is the lowest concentration of a VOC that can be quantitatively measured with acceptable accuracy and precision (Wang & Austin, 2006; Eurachem, 2025).

While the LOD merely indicates the presence of an analyte, the LOQ ensures that the VOC concentration can be determined with statistical confidence. Typically, LOQ is defined as a multiple (e.g., 10 times) of the standard deviation of the baseline noise or the calibration curve residuals.

Recovery measures the accuracy of the method by assessing how efficiently VOCs can be collected, desorbed, and quantified from air samples (Gallego et al., 2011; Eurachem, 2025). This is determined by spiking known amounts of VOCs onto sorbent tubes or into air sampling canisters, followed by analysis and comparison with the expected values. High recovery values indicate minimal losses during sampling, desorption, and analysis, ensuring reliable

quantitative results. Together, these parameters form the foundation of method validation, ensuring that the analytical technique employed for VOC analysis in ambient air is robust, sensitive, and precise.

By systematically evaluating repeatability, LOD, LOQ, and recovery, researchers can establish the credibility of their GC-MS method, making it suitable for air quality monitoring, exposure assessment, and regulatory reporting.

Table 3. Method validation for the analysis of Volatile Organic Compounds in ambient air

Compound name	Repeatability								LOD (ng)	LOQ (ng)	Recovery (%)
	Intra-day 1.6 ng	RSD (%) n = 6	Inter-day 1.6 ng	RSD (%) n = 6	Intra-day 10 ng	RSD (%) n = 6	Inter-day 10 ng	RSD (%) n = 6			
Dichloroethene	1.56	3.11	1.65	4.27	9.98	2.67	10.09	3.48	0.15	0.38	94
Cis - 1,2 dichlorethene	1.64	3.68	1.69	4.84	9.86	2.94	9.74	3.52	0.18	0.42	87
1,1 - Dichloroethane	1.57	3.21	1.66	3.84	9.62	2.47	10.41	3.80	0.12	0.85	93
Bromochloromethane	1.57	3.15	1.66	3.39	9.86	2.94	9.60	3.50	0.11	0.88	82
Chloroform	1.62	3.99	1.61	4.80	9.95	2.57	9.52	3.69	0.11	0.82	105
1,1,1 - Trichloroethane	1.63	4.09	1.54	4.16	9.98	2.67	10.30	3.98	0.13	0.72	98
1,2 - Dichloroethane	1.58	3.17	1.58	4.67	9.73	2.41	9.51	3.93	0.18	0.79	121
Carbon tetrachloride	1.63	2.70	1.62	3.84	10.03	2.28	9.74	4.31	0.13	0.75	91
Benzene	1.64	3.65	1.66	4.58	9.65	2.29	9.75	3.45	0.08	0.70	88
Dibromomethane	1.63	4.48	1.56	4.06	10.26	2.85	9.47	3.51	0.16	0.47	108
1,2 - Dichloropropane	1.58	4.01	1.55	5.00	9.97	2.15	9.61	3.42	0.14	0.73	117
Trichloroethene	1.64	4.47	1.67	3.22	9.74	2.56	9.76	3.59	0.12	0.60	93
Bromodichlorometh.	1.59	3.94	1.52	4.33	9.89	2.12	10.38	3.20	0.09	0.27	95
cis13-Dichloropropene	1.60	3.44	1.60	3.76	9.83	2.43	10.27	4.40	0.10	0.80	84
tra13-dichloropropene	1.63	4.04	1.67	4.22	10.04	2.17	10.47	3.70	0.14	0.88	118
Toluene	1.62	3.29	1.53	4.04	10.24	2.53	9.94	3.50	0.10	0.30	105
1,1,2 - trichloroethane	1.63	3.90	1.67	3.77	10.27	2.64	10.49	4.10	0.17	0.54	110
1,3 – Dichloropropane	1.58	3.89	1.57	3.89	9.69	2.45	9.53	3.22	0.09	0.36	101
Dibromochlorometh.	1.56	3.29	1.63	4.70	9.80	2.70	10.47	4.41	0.11	0.39	108
1,2-Dibromoethane	1.62	4.21	1.65	4.08	9.99	2.70	9.84	3.15	0.12	0.50	116
Tetrachloroethene	1.63	3.31	1.68	3.38	10.15	2.51	9.49	4.35	0.10	0.52	98
Chlorobenzene	1.58	2.62	1.58	5.08	9.69	2.63	9.48	4.06	0.09	0.56	102
1,1,1,2-Tetrachloroeth.	1.56	3.62	1.57	3.77	9.88	2.95	10.09	4.02	0.17	0.65	88
Ethylbenzene	1.61	4.41	1.63	3.31	9.90	2.18	9.44	3.26	0.09	0.30	105
mp-Xylene	1.58	2.73	1.51	4.35	10.27	3.12	9.96	4.12	0.10	0.63	121
Bromoform	1.56	3.18	1.53	5.05	9.65	2.48	9.62	4.36	0.15	0.80	94
Styrene	1.60	3.78	1.54	3.95	10.13	3.09	9.47	3.53	0.14	0.63	98
o-Xylene	1.57	2.52	1.67	3.87	9.99	2.74	10.02	3.21	0.15	0.57	124
1,1,2,2-Tetrachloroeth.	1.57	4.31	1.63	3.76	10.22	2.32	9.76	3.97	0.09	0.89	86
1,2,3Trichloropropane	1.64	3.92	1.59	3.91	10.12	2.35	9.50	3.17	0.16	0.72	79
Isopropilbenzene	1.56	4.29	1.65	4.12	9.81	2.73	10.01	4.24	0.16	0.44	105
Bromobenzene	1.61	3.38	1.56	4.90	10.28	2.77	9.65	3.14	0.15	0.75	119
o-Chlorotoluene	1.64	3.23	1.68	4.87	9.81	3.14	10.55	4.14	0.09	0.25	116
n-Propylbenzene	1.56	4.24	1.67	4.38	10.19	2.40	9.72	3.51	0.09	0.56	118
4-Chlorotoluene	1.57	3.04	1.58	4.83	10.04	3.03	9.87	3.95	0.11	0.27	101
1,3,5-Trimethylbenz.	1.58	2.63	1.54	3.92	9.70	2.44	9.63	3.68	0.12	0.58	94
S-butylbenzene	1.57	3.43	1.66	4.59	9.79	2.23	9.74	3.32	0.13	0.56	98
1,4-Dichlorobenzene	1.63	3.88	1.59	5.01	10.18	2.33	10.12	4.21	0.10	0.37	110
p-Cymene	1.63	4.49	1.64	3.65	10.09	2.21	9.66	4.03	0.16	0.68	79
1,2-Dichlorbenzene	1.57	2.64	1.53	3.92	10.25	2.63	9.61	3.92	0.10	0.37	89
n-Butylbenzene	1.58	3.06	1.67	4.01	9.72	2.97	10.52	3.70	0.14	0.52	116
1,2,4-Trichlorobenz.	1.57	4.47	1.56	4.55	9.96	2.57	9.85	3.38	0.13	0.29	105
Naphthalene	1.62	3.39	1.66	3.74	10.25	2.72	9.57	4.54	0.13	0.69	87
1,2,3-Trichlorobenz.	1.59	3.22	1.53	3.50	10.25	2.61	9.74	3.92	0.14	0.35	101
Hexachlorobutadiene	1.56	3.44	1.59	3.21	10.08	2.93	9.94	3.65	0.08	0.82	92

The validation of the analytical method used for the determination of volatile organic compounds (VOCs) in ambient air has demonstrated high performance in terms of precision, repeatability, and sensitivity. The obtained values for the limits of detection (LOD) and limits of quantification (LOQ) indicate an adequate capability to identify and quantify compounds at

low concentrations, which is essential for ambient air monitoring (Demeestere et al., 2008; Kim & Park, 2020;). Furthermore, the achieved recovery rates, falling within an optimal range, confirm the accuracy of the method and the reliability of the results (Wang et al., 2018). Intra and inter-day repeatability, expressed through the relative standard deviation (RSD), has shown the stability of the method under various analytical conditions, further demonstrating its robustness. These aspects are crucial for applying the method in long-term monitoring studies aimed at assessing population exposure to VOCs and their impact on air quality and human health.

In conclusion, the validated TD-GC-MS method exhibits analytical characteristics that comply with international standards for VOC analysis in ambient air. Its high sensitivity and precision make it a reliable tool for monitoring volatile organic compounds in urban and industrial environments, providing essential data for the development of air pollution mitigation strategies and the protection of public health (Chung et al., 2019; Zou & Yang, 2022).

Field Monitoring of Volatile Organic Compounds (VOCs)

Field monitoring of volatile organic compounds (VOCs) is essential for assessing air quality and understanding the spatial and temporal distribution of these pollutants in different environments. The selection of monitoring sites, sampling techniques, and analytical methods plays a crucial role in obtaining representative and reliable data.

Preparation of Tenax Tubes: Calibration and Verification

The Acti-VOC pump was calibrated to a flow rate of 200 mL/min using the 7000 Ellutia electronic flowmeter to ensure accuracy and consistency in sample collection. Prior to conditioning, each Tenax tube was individually inspected to verify proper airflow and sorbent integrity (Figure 7).

The recorded parameters were systematically analysed, and the data distribution, along with the potential variability for the Tenax tubes, was evaluated and presented in Figure 8 to ensure reliability and reproducibility in the adsorption process.

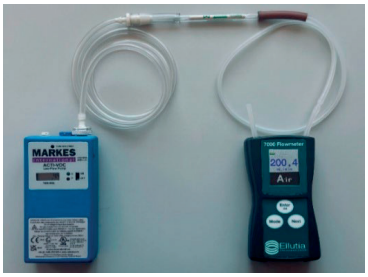

Figure 7. Flow Rate adjustment and flow monitoring

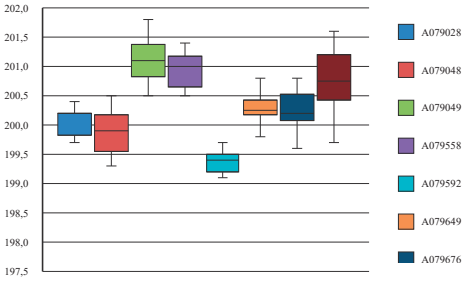

Figure 8. Flow assessment for Tenax TA tubes

To ensure consistency and verify the results, the same experiment was conducted on tubes containing both Tenax and Carboxen 1018, following the same procedure as for the tubes containing only Tenax. The data for the Tenax/ Carboxen 1018 tubes are presented in Figure 9, where the distribution and variability of the recorded parameters are analysed.

The flow rate measurements for the Tenax-only tubes and the combined Tenax and Carboxen tubes showed consistent performance throughout the experiments. While the Tenax-only tubes exhibited stable flow characteristics within the expected range, the inclusion of Carboxen did not significantly affect the flow dynamics.

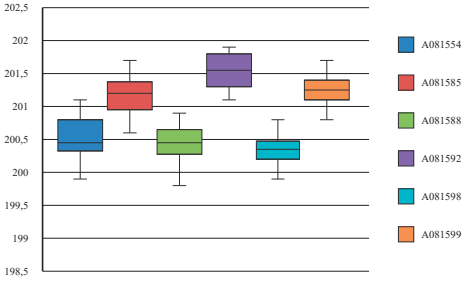

Figure 9. Flow assessment for TA Tubes/Carboxen1018

Both configurations demonstrated reliable flow rates, making them suitable for the collection of volatile organic compounds (VOC) from ambient air. These results confirm that both types of tubes are appropriate for accurate VOC sampling from ambient air, with minimal impact on the flow rate.

Conditioning of Tenax and Tenax/Carboxen Tubes for VOC Analysis

Tenax and Tenax/Carboxen tubes were conditioned using a Shimadzu Thermodesorber 30R. Desorption was performed at a temperature of 280°C and a flow rate of 70 mL/min for 20 minutes (Maria, 1996; SR EN 14662-4, 2005). The conditioning process was carried out in the reverse direction of the sampling flow to ensure complete desorption of any retained compounds and to prepare the tubes for subsequent analysis (SR EN 14662-5, 2005). According to the performed experiments, this method effectively removed any potential contaminants and ensured the integrity of the tubes prior to their use in VOCs sampling.

System checks and quality control

In order to ensure the reliability and accuracy of TD-GC-MS measurements, routine system checks, and quality control procedures were performed daily or after every 20 thermal desorption tubes analysed. These procedures included instrument warm-up, carrier gas flow verification, vacuum pressure monitoring, and mass spectrometer performance assessment. BFB (4-bromofluorobenzene) tuning check (30026; Batch A0189204) was conducted in full scan mode according to the requirements of EPA Method TO-17, to verify mass calibration, resolution, and detector sensitivity. Ion abundance criteria, as outlined in Table 4, were applied to specific fragment ions and the tune was accepted only when all values fell within the predefined range.

Moreover, using the system performance mix (30075; Batch A0189066), retention times, peak heights and area were verified for the following compounds: Bromoform, Chlorobenzene, 1,1-Dichloroethane and 1,1,2,2-Tetrachloroethane. These parameters were evaluated to ensure consistency and accuracy of the system performance and analytical method in detecting analytes. Both BFB tuning and system performance checks were performed at 10 ng to ensure the precision and sensitivity of the system during analysis of target compounds in the environmental samples.

Table 4. Ion abundance criteria for 4-bromofluorobenzene

m/z	Spectrum check criteria
50	15 to 40 % of 95 mass 95
75	30 to 60 % of mass 95
95	Base peak, 100% relative abundance
96	5 to 9 % of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9 % of mass 174
176	95 to 101 % of mass 174
177	5 to 9% of mass 176

Monitoring Sites and Sampling Techniques for VOC Assessment

The placement of monitoring stations for volatile organic compounds (VOCs) is a critical step in assessing air quality. In this study, VOC samples were collected in two distinct locations within the Jiu Valley region: the industrial area near the Lonea mine and the urban/pedestrian area of the Petroșani city center. The sampling points were selected to evaluate VOC concentrations in both an industrial environment and an urban area with high pedestrian traffic.

At each of these points, multiple sequential samples were collected using both Tenax and Tenax/Carboxen tubes. For each location, a blank sample was also collected using one of the tubes to assess potential contamination during the sampling process. The active sampling was conducted with the Acti-VOC pump at a flow rate of 200 mL/min, and each sample was collected for a 15-minute period. After the sampling process, the tubes were analysed using Thermal Desorption Gas Chromatography-Mass Spectrometry (TD-GC-MS) to quantify and identify the VOCs present in the ambient air. This approach ensured that a comprehensive analysis of VOC levels was conducted at both the industrial and urban/pedestrian sites, providing valuable insights into the air quality in these different environments. The results of these analyses, including VOC concentrations at the respective sites, are presented in Figure 10.

Together, these parameters form the foundation of method validation, ensuring that the analytical technique employed for VOC analysis

in ambient air is robust, sensitive, and precise. By systematically evaluating repeatability, LOD, LOQ, and recovery, researchers can establish the credibility of their GC-MS method, making it suitable for air quality monitoring, exposure assessment, and regulatory reporting.

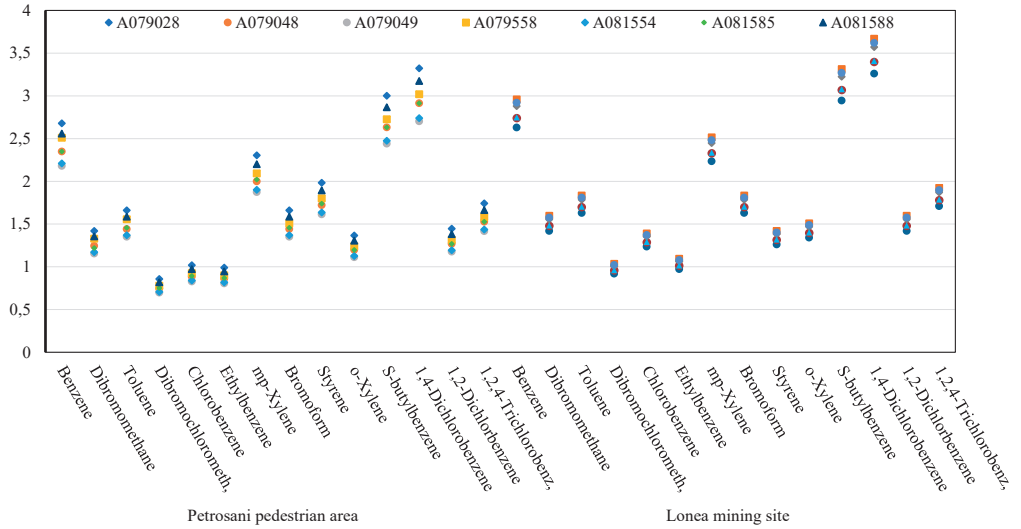

Figure 10. Analysis of Volatile Organic Compounds in ambient air on Petrosani and Lonea mining site

The measured concentrations of the investigated VOCs reveal discernible differences between the Petroșani pedestrian area (left cluster) and the Lonea mining site (right cluster). Each compound is represented by multiple data points (A079028, A079048, A079049, A079558, A081554, A081585, and A081588), thereby illustrating both inter-sample variability and site-specific emission characteristics.

Certain aromatic hydrocarbons (e.g., p-xylene, ethylbenzene, and benzene) appear more pronounced in the urban/pedestrian environment, potentially reflecting the influence of vehicular traffic, commercial activities, and population density. Conversely, the mining area exhibits elevated or comparable concentrations of halogenated compounds, such as 1,2-dichloroethane, suggesting contributions from industrial or mining-related processes. The overall range of values, extending from roughly 1.0 to 3.5 $\mu g/m^3$ underscores the necessity for robust sampling strategies and precise analytical methods to capture the nuances of VOC distribution.

Moreover, the fluctuations in measured concentrations highlight the impact of temporal factors (e.g., time of day, operational cycles) and microclimatic conditions (e.g., temperature, wind speed) on ambient VOC levels. This dataset thus reinforces the importance of employing comprehensive monitoring protocols, encompassing both spatial and temporal dimensions, to inform targeted mitigation measures and support evidence-based policymaking in air quality management.

CONCLUSIONS

This research aimed to develop and validate an optimized TD-GC-MS method for monitoring VOCs in ambient air. The applied methodology, which combined thermal desorption with gas chromatography-mass spectrometry and incorporated the use of internal standards and certified reference materials, ensured high analytical accuracy and traceability in calibration. The optimized method demonstrated excellent sensitivity - evident in its low detection and quantification limits - allowing for the reliable identification of VOCs at trace levels, as well as high precision and repeatability, with minimal variability observed in both short and long-term analyses. Additionally, the recovery rates obtained during

the method validation fell within optimal ranges, further confirming the accuracy and reliability of the analytical procedure. These performance characteristics comply with international standards in the field, which underscores the robustness of the method and its suitability for continuous air quality monitoring.

Key findings and contributions of this study include the provision of a robust, validated analytical solution for the systematic monitoring of VOCs in urban and industrial environments, thereby generating critical data for air pollution assessments. The field application of the optimized TD-GC-MS method confirmed its utility in obtaining detailed information on the spatial and temporal distribution of organic pollutants, which is essential for identifying emission sources and population exposure levels. Such information is highly relevant to public health, as more precise and reliable VOC monitoring contributes to a better understanding of the relationships between pollutant exposure and adverse health effects (e.g., respiratory, cardiovascular, or neurological issues), thereby supporting the development of risk mitigation strategies. Moreover, this study has significant implications for environmental regulations. The proposed method, which aligns with international guidelines (e.g., Eurachem), can be employed by regulatory bodies and laboratories to ensure compliance with air quality standards and to inform environmental policy. Overall, the successful validation of this optimized TD-GC-MS method represents a significant advancement in atmospheric pollution monitoring, offering a dependable tool for protecting both the environment and public health. The method proves to be highly effective and reliable for VOC monitoring in ambient air, providing exceptional sensitivity and precision, even at trace concentrations. Given its robustness, it is strongly recommended for continuous air quality assessments, particularly in urban and industrial environments, where accurate tracking of volatile organic compounds is crucial for public health protection and compliance with environmental regulations.

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