New procedure for the examination of the degradation of volatile organonitrogen compounds during the treatment of industrial effluents

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We present a new procedure for the determination of 32 volatile organonitrogen compounds in samples of industrial effluents with a complex matrix. The procedure, based on dispersive liquid–liquid microextraction followed by gas chromatography with nitrogen-phosphorus and mass spectrometric detection, was optimized and validated. Optimization of the extraction included the type of extraction and disperser solvent, disperser solvent volume, pH, salting out effect, extraction, and centrifugation time. The procedure based on nitrogen-phosphorus detection was found to be superior, having lower limits of detection (0.0067–2.29 μg/mL) and quantitation as well as a wider linear range. The developed procedure was applied to the determination of content of volatile organonitrogen compounds in samples of raw effluents from the production of bitumens in which 13 compounds were identified at concentrations ranging from 0.15 to 10.86 μg/mL and in samples of effluents treated by various chemical methods.

KEYWORDS

dispersive liquid-liquid microextraction, gas chromatography, postoxidative effluents, volatile organonitrogen compounds, wastewater

1 | INTRODUCTION

Volatile organonitrogen compounds (VNCs), which include, among others, amines, nitro compounds, nitriles, and heterocyclic nitrogen compounds, play an important role in pollution of aqueous environment due to their high toxicity, stability, and the ability to accumulate in links of the food chain. VNCs are also hazardous to human health, being irritants of the respiratory tract, skin, and mucous membranes. In aqueous environment they can be converted to nitrosamines, a significant fraction of which has been classified as carcinogens [1–3]. VNCs can enter the environment from anthropogenic sources, such as refinery and petrochemical industry [4–6], pharmaceutical industry [7,8], dye industry as well as plastics [9], antioxidants, and explosives industries. Furthermore, VNCs can be formed in drinking water as a result of water chlorination [10,11]. Industrial effluents containing high concentrations of VNCs pose a serious problem due to their malodorousness at a low odor recognition threshold and a high level of toxicity. Effluents from the production of bitumens are an example of strongly toxic effluents containing volatile organic compounds, including organosulfur, oxygenated, and organonitrogen compounds. Due to their specific properties, these effluents pose numerous problems during their treatment [12–16].

As a result of the need to determine VNCs at low concentration levels, very sensitive, and selective analytical techniques have to be used. At present, chromatographic techniques are commonly employed in the analysis of water and wastewater, including LC [17], CE [18], and especially GC owing to its high resolution and the possibility of optimization of a number of separation and detection parameters. However, the use of GC can lead to a number of problems due to specific physicochemical properties of some VNCs, such as their high volatility, polarity, basic nature, and trace concentrations in samples having a very complex matrix. In addition, the presence of hydrogen bonding in aliphatic amines poses additional problems, including peak tailing and the wall memory effect, i.e. the possibility of adsorption of analytes on the walls of containers used in the investigations and their subsequent desorption during the next analysis [19]. Therefore, analytes are often derivatized to improve

Abbreviations: DCM, dichloromethane; DLLME, dispersive liquid–liquid microextraction; NPD, nitrogen-phosphorus detector; VNC, volatile organonitrogen compounds

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their chromatographic properties using various derivatizing agents, such as benzenesulfonyl chloride [20], iodine [21], or pentafluorobenzaldehyde [22]. However, derivatization is time-consuming and tedious and it can result in the formation of unintended side products and contamination of a sample, thus becoming an additional source of errors [23]. Another way of improving sensitivity is the use of selective detectors, such as the nitrogen-phosphorus detector (NPD) [24], chemiluminescent nitrogen detector (CLND) [25], or surface ionization detector (SID) [26], which enable the determination of a large number of VNCs. However, despite the possibility of obtaining satisfactory sensitivity, direct injection of industrial effluents onto a chromatographic column is not recommended due to the presence of inorganic salts and nonvolatile matrix components. Consequently, a sample preparation step resulting in analyte isolation and enrichment is a must. Modern trends in sample preparation favor extraction techniques that minimize the use of organic solvents are simple, rapid, and automatable. All these requirements are met by static headspace analysis (SHS) [27] and dynamic headspace analysis (DHS), but these techniques are applicable to the analysis of compounds with boiling points not exceeding 150°C. To determine a wider variety of volatile organic compounds, techniques such as SPE [28], SPME [29], or headspace SPME can be used. However, these sample preparation methods are time consuming that disqualifies them for routine analyses. Dispersive liquid–liquid microextraction (DLLME), proposed by Rezaee in 2006 [30], overcomes this problem and is also considered to be a green analytical technique [30].

The paper discusses and compares two new procedures for the determination of volatile organonitrogen compounds in industrial effluents based on DLLME combined with GC–MS or GC–NPD. To demonstrate applicability of the developed procedure, the results of determination of VNC content in effluents treated by various chemical methods were compared.

2 | MATERIALS AND METHODS

2.1 | Materials

Gases: hydrogen–purity 5,5N from a PGXH2 500 Hydrogen Generator (Perkin Elmer, USA), helium purity 5,5N (Linde Gas, Poland), air purity 5,0N generated by a DK50 compressor with a membrane dryer (Ekkom, Poland) and further purified by a GC3000 zero air generator (Perkin Elmer, USA), nitrogen purity 5N (Linde Gas, Poland). Reagents: dichloromethane (POCH, Poland), carbon tetrachloride (Merck, Germany), chloroform (POCH, Poland), methanol (POCH, Poland), acetone (for HPLC, POCH, Poland), isopropanol (POCH, Poland), NaCl (POCH, Poland), sodium hydroxide (POCH, Poland). Standards: pyridine, 3-methylpyridine, 4-methylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, acetanilide, nitromethane, nitrobenzene, 1-nitropropane, 2-nitrotoluene, 4-nitrotoluene, 2,6-dinitrotoluene, 1,2-dinitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2-nitrophenol, 4-nitrophenol, 2-aminophenol, *p*-toluidine, amylamine, hexylamine, heptylamine, 2-ethyl-1-hexylamine, aniline, *N*-methylaniline, *N*,*N*-diethylaniline, diethanolamine, pyrrole, pyrazole, indole, quinoline, formamide; internal standard: 2-chloropyridine (Sigma–Aldrich, USA).

2.2 | Real samples

Samples of postoxidative effluents from the production of petroleum bitumen 20/30 from the vacuum residue of REBCO (Russian Export Blend Crude Oil) and REBCO/Kirkuk (88:12 w/w) (blend of Russian and Iraqi crude) mixture were collected from a plate separator that separated the condensed organic phase from the aqueous phase. The investigations presented in this paper were carried out for the aqueous phase of raw effluent as well as for the effluents subjected to various treatments, including hydrogen peroxide and Oxone® reagent (potassium peroxymonosulfate). The characteristics of postoxidative effluents were described in previous papers [15,16], while a detailed description of treatment processes and their effectiveness will be the subject of future papers.

2.3 | Apparatus

GC was performed using a Perkin Elmer Autosystem XL gas chromatograph with an autosampler and nitrogen-phosphorus (NPD) as well as flame ionization (FID) detector (PerkinElmer, USA); an HP 5890 II gas chromatograph with an HP 5972A mass spectrometer (Hewlett-Packard, USA); capillary columns: DB-624 (60 m × 0.32 mm × 1.0 μm) (Agilent, USA) and Rxi-624Sil MS (60 m × 0.25 mm × 1.40 μm) (Restek, USA); TurboChrom 6.1 (PerkinElmer, USA) and Chemstation (Agilent, USA) with NIST 05 and Wiley 8.0 mass spectral libraries, and an EBA 8S centrifuge (Hettich, Germany).

2.4 | Procedures

2.4.1 | Dispersive liquid–liquid microextraction

For the optimized DLLME conditions, the analytical procedure was as follows: a sample of the effluent (10 mL) was placed in a 12-mL vial along with 10 μL of a 10% solution of 2-chloropyridine in acetone, 0.4 mL of acetone and 0.5 mL of dichloromethane. Next, the sample was shaken vigorously for 20 s, followed by centrifugation at 4000 rpm for 5 min. A volume of 250 μL of the sedimented organic phase was then transferred to 2 mL vials equipped with 300 μL micro inserts. The vials were placed in an autosampler. Finally, 2 μL of the extract was analyzed by GC.

2.4.2 | Quantitative analysis

Quantitative analysis was carried out using the internal standard method (2-chloropyridine). A stock solution containing 32 compounds at concentrations of about 1000 μg/mL was prepared in acetone. Standard solutions at concentrations 0.05, 0.5, 5, and 50 μg/mL (GC–NPD) and 0.5, 1, 5, 10, and 50 μg/mL (GC–MS) were prepared from the stock solution by serial dilution with deionized water. Further procedure was carried out according to Section 2.4.2.

2.4.3 | Chromatographic conditions

Two systems: GC–MS and GC–NPD were used in the investigations. In addition, GC–FID was employed during optimization of DLLME conditions. The following conditions were used for the GC–NPD system: injection port temperature 270°C; injection mode: split (10:1); injection volume 2 μL; detector temperature 270°C; detector gases flow rates: air 100 mL/min, hydrogen 2 mL/min: carrier gas (helium) flow rate 2 mL/min; oven temperature program: 60°C (5 min)–ramped at 7°C /min to 260°C (20 min). In the experiments making use of GC–FID the carrier gas was nitrogen (1 mL/min); detector gases flow rates: air 450 mL/min, hydrogen 40 mL/min. The remaining parameters were the same as in the GC–NPD system. In the GC–MS system the carrier gas was hydrogen (1 mL/min); ion source temperature (EI, 70 eV) 200°C, GC–MS transfer line temperature 300°C, while the remaining conditions were the same as in the GC–NPD system.

2.4.4 | Analysis of real samples

Samples of raw effluents were analyzed without pH adjustment while for treated effluents the pH was adjusted to 11 (the pH found to be optimal during the optimization step) using a 2.0 M NaOH solution. Further steps of the procedure were carried out according to Section 2.4.2.

2.4.5 | Method validation

LOD and quantitation: please refer to Supporting Information (Section S.1).

Linear range: The linearity of calibration curve carried out using an internal standard was estimated using the correlation coefficient (r). To confirm an appropriate selection of the linear range, a standard residual analysis was performed [31]. Recovery (R) was calculated from Eq. (1).

$$R\ [\%] = \frac{C_{\text{quant}}}{C_{\text{expect}}} \cdot 100\% \qquad (1)$$

where

$C_{\text{quant.}}$ – found analyte concentration in spiked sample [μg/mL]

$C_{\text{expect.}}$ – analyte concentration added as spike [μg/mL].

3 | RESULTS AND DISCUSSION

3.1 | Optimization of dispersive liquid–liquid microextraction

The dispersive liquid–liquid microextraction procedure was optimized by comparing chromatographic peak areas for six compounds, namely, pyridine, pyrazole, heptylamine, 2-aminophenol, diethanolamine, and 1,3-dinitrobenzene, for which the effect of variation in individual extraction parameters was investigated. DLLME conditions were optimized in terms of kind of extraction solvent, kind, and volume of disperser solvent, salting out effect, pH, extraction time, and time of centrifuging. Three extraction solvents: dichloromethane (DCM), chloroform (CF), and carbon tetrachloride (TCM) and three disperser solvents: acetone (AC), methanol (MeOH), and isopropanol (IPA) were tested. The disperser solvent volume was varied from 0 to 1.2 mL. The amount of NaCl added ranged from 0 to 2.0 g for 10 mL of the samples. The pH of the effluents was fixed at 7, 11, and 14 using a 2.0 M NaOH solution. In addition, centrifugation time was varied from 3 to 12 min at a centrifugation rate of 4000 rpm while extraction time was set at 20, 40, 60, and 90 s. The effect of variation of individual parameters on extraction yield was estimated by comparing peak areas for the selected analytes.

3.1.1 | Selection of extraction and disperser solvent

The effect of kind of extraction and disperser solvent on extraction effectiveness was investigated by testing three extraction and three disperser solvents (Supporting Information Fig. S1). The experimental results revealed that the extraction solvent had the greatest effect on extraction efficiency while the kind of disperser solvent had only a minor effect [32,33]. Carbon tetrachloride had the highest extraction efficiency for heptylamine and satisfactory extraction efficiency for 2-aminophenol and 1,3-dinitrobenzene while for the other two analytes the extraction efficiency was the lowest. The highest extraction effectiveness for heterocyclic organonitrogen compounds (pyridine and pyrazole) was observed for chloroform. However, for the majority of analytes dichloromethane proved to be the most effective extraction solvent. Consequently, in further experiments 0.5 mL of DCM was used for extraction. This volume was chosen due to the use of an autosampler during the final determination step. Autosampler enables routine analyses of industrial effluents. The same volume of the extraction solvent has been used in automated DLLME systems [34].

A number of DLLME procedures made use of acetonitrile as a disperser solvent, since it provided the highest extraction effectiveness for organonitrogen compounds. However, in the present study acetonitrile was not considered due to the use of a selective NPD detector and the possibility of coelution of analytes with the disperser solvent [35]. Among the disperser

solvents tested, isopropanol provided the smallest enrichment factor while methanol and acetone had similar values of *R*. Since acetone was used in previous studies [12,14], it was selected as the disperser solvent.

3.1.2 | Volume of disperser solvent

The effect of disperser solvent (acetone) volume on extraction yield was examined for volumes equal to 0, 0.2, 0.4, and 0.8 mL (Supporting Information Fig. S2). An increase in peak areas was observed for the majority of analytes with the volume of acetone up to 0.4 mL. Further increase in volume resulted in a decrease in extraction yield due to an increase of organic phase volume and solubility of the analytes in the sample phase. Complete absence of a disperser solvent or an insufficient volume of it brings about ineffective dispersion of the extraction solvent in a sample resulting in a lowered recovery of the analytes.

3.1.3 | pH

pH is an important parameter that can have a significant effect on the analyte recovery. Consequently, extraction yields were investigated at three pH values: 7, 11, and 14. pH values below 7 were not examined since the majority of the analytes have a basic character and at pH values less than 7 the amine groups would be protonated thus shifting equilibrium toward the aqueous phase. The greatest changes in extraction yield were observed for *n*-heptylamine for which the maximum yield was found at pH 11 and further increase in pH had no effect on extraction yield. A similar effect of pH for aliphatic amines was observed in other papers that is consistent with theoretical predictions [22,35]. For the other groups of compounds pH had no significant effect on extraction yield. Therefore, further investigations were carried out in a basic medium (pH 11). This pH value is also favorable from a standpoint of properties of primary effluents from the production of bitumens that have a basic nature with a pH ranging from 10.5 to 11.0 [35,36]. Hence, analyses of raw effluents can be carried out without pH adjustment that eliminates one step in the sample preparation procedure.

3.1.4 | Extraction time

The time of extraction, i.e. the time of shaking a sample with the disperser and extraction solvent was studied for four time values: 20, 40, 60, and 90 s (Supporting Information Fig. S4). The results obtained demonstrate that in the investigated range extraction time has no effect on extraction yield. This is consistent with the principle of DLLME in which extraction process takes several seconds [33]. Consequently, a 20 s extraction time was selected as the optimum value.

3.1.5 | Centrifugation time

The effect of time of centrifugation was examined over the range 3–12 min at a speed of 4000 rpm (Supporting Information Fig. S5). A slight improvement in extraction yield was observed after 5 min of centrifugation and a further increase in time had no significant effect on extraction yield. Similar effects were also observed in other studies [35]. Centrifugation speed of 4000 rpm is routinely used in DLLME, and its further increase does not improve extraction yield of analytes.

3.1.6 | Salting out

To examine the effect of salting out on VNC extraction yield, 0, 0.5, 1, and 2 g of sodium chloride were added to 10 mL of the samples. The results obtained reveal different effects of the same amount of NaCl on extraction yield for different groups of compounds (Supporting Information Fig. S6). For 2-aminophenol, heptylamine, and 1,3-dinitrobenzene the extraction yield decreased with an increase in salt concentration while the opposite effect was observed for pyridine, pyrazole, and diethanolamine. Furthermore, after addition of 2 g of NaCl phase inversion, i.e. appearance of the organic phase over the aqueous phase was observed due to an increase in density of the aqueous phase. Thus, further investigations were carried out without salt addition.

3.2 | Validation and comparison of procedures

The determination of 32 volatile organonitrogen compounds was carried out using two detection systems: DLLME–GC–NPD and DLLME–GC–MS. In both cases the internal standard method was used for quantitative analysis. 2-Chloropyridine was selected as the IS based on similarity of its physicochemical properties to those of the analytes as well as on its absence from the investigated samples. Calibration of the analytes in the GC–NPD system was based on four concentrations: 0.05, 0.5, 5, and 50 μg/mL, whereas the GC–MS calibration excluded concentration 0.05 μg/mL owing to a lower sensitivity of the detector and was based on the following concentrations: 0.5, 1, 5, 10, and 50 μg/mL. For the GC–MS system two characteristic ions were selected for each analyte: m/z_{int} that was used for peak integration and m/z_{id} that was used for identification of the analytes. A list of characteristic ions is compiled in Supporting Information Table S1.

The procedure based on GC–NPD has much lower limits of detection compared to GC–MS. The lowest LOD values were obtained for indole (0.0067 μg/mL) and for pyridine and its derivatives (0.031–0.050 μg/mL) as well as for aliphatic amines (0.017–0.086 μg/mL) and aliphatic nitro compounds (0.017–0.043 μg/mL). On the other hand, the highest LOD values were found for 2,4-dinitrotoluene and acetanilide. For the GC–MS system the LOD values were higher by an order of magnitude and in some cases by two orders of magnitude. One of the reasons for such high LOD values is the lack of characteristic ions (*m/z*) for some analytes. Consequently, to ensure sufficient selectivity, ions with lower intensity have to be chosen that causes inferior sensitivity. In addition, peak

TABLE 1 Compilation of calibration parameters for analytes using GC-NPD

Compound	t_R [min]	Calibration curve	LOD [µg/mL]	LOQ [µg/mL]	R^2	RSD [%][a]	R [%][a]
Nitromethane	6.98	$y = 0.8129x + 0.0110$	0.043	0.13	0.9988	3.20	100.93
Amylamine	13.05	$y = 3.8077x - 0.0045$	0.020	0.060	0.9999	1.34	103.10
Pyridine	14.02	$y = 2.1262x + 0.0094$	0.037	0.11	0.9997	2.26	107.71
1-Nitropropane	15.99	$y = 2.5717x + 0.0006$	0.017	0.051	0.9999	5.29	97.81
Pyrrole	16.58	$y = 0.1587x + 0.0006$	0.87	2.61	0.9999	2.34	105.61
3-Methylpyridine	18.34	$y = 2.3018x + 0.0098$	0.048	0.14	0.9997	4.00	111.88
4- Methylpyridine	18.41	$y = 2.2511x + 0.0074$	0.046	0.14	0.9996	3.55	109.12
Pyrazole	18.62	$y = 0.2021x + 0.0013$	0.90	2.70	0.9999	3.62	105.59
2,4-Dimethylpyridine	20.34	$y = 3.6642x + 0.0183$	0.031	0.093	0.9993	3.31	126.37
2,4,6-Trimethylpyridine	21.85	$y = 2.3076x + 0.0081$	0.050	0.15	0.9996	2.60	115.34
2-Ethyl-1-hexylamine	22.80	$y = 2.5302x + 0.0115$	0.056	0.17	0.9995	3.17	117.72
Aniline	23.06	$y = 2.5692x + 0.0054$	0.14	0.42	0.9999	3.08	98.11
Hexylamine	25.13	$y = 3.5318x + 0,0167$	0.043	0.13	0.9997	1.70	109.25
N-methylaniline	25.42	$y = 1.3348x + 0.0119$	0.33	0.99	0.9961	2.73	121.23
Formamide	25.76	$y = 4.2908x + 0.0095$	0.094	0.28	0.9997	3.89	111.02
Heptylamine	26.18	$y = 5.1001x + 0.0216$	0.086	0.26	0.9993	3.53	123.22
Nitrobenzene	28.01	$y = 1.1463x + 0.0079$	0.081	0.24	0.9991	3.02	118.32
p-toluidine	28.44	$y = 3.1900x + 0.0257$	0.041	0.12	0.9982	3.07	84.83
o-nitrophenol	28.57	$y = 0.7300x - 0.0042$	0.11	0.33	0.9990	3.20	119.68
2-Nitrotoluene	29.46	$y = 0.6473x - 0.0084$	0.81	2.43	0.9966	2.67	107.25
N,N-diethylaniline	29.64	$y = 0.6387x + 0.0039$	0.62	1.86	0.9987	4.78	123.89
Quinoline	29.77	$y = 3.4126x + 0.0213$	0.033	0.099	0.9980	4.72	122.41
2-Aminophenol	30.09	$y = 0.6317x + 0.0138$	0.38	1,14	0.9988	3.40	120.54
4-Nitrotoluene	32.02	$y = 0.4580x - 0.0033$	0.78	2.34	0.9959	2.86	62.57
Indole	32.34	$y = 2.1854x + 0.0014$	0.0067	0.020	0.9996	3.81	111.05
Acetanilide	34.27	$y = 0.2489x - 0.0032$	1.94	5.82	0.9973	4.51	74.24
Diethanolamine	34.76	$y = 0.6279x + 0.0020$	0.28	0.84	0.9998	5.17	107.94
2,6-Dinitrotoluene	34.86	$y = 0.2540x + 0.0003$	2.29	6.87	0.9967	5.64	64.43
o-Dinitrobenzene	35.51	$y = 0.4234x + 0.0048$	0.25	0.75	0.9979	4.53	128.34
m-Dinitrobenzene	36.00	$y = 0.4140x + 0.0010$	0.26	0.78	0.9985	3.22	131.38
p-dinitrobenzene	37.92	$y = 0.4419x + 0.0056$	0.25	0.75	0.9944	3.51	136.23
p-nitrophenol	36.26	$y = 0.6387x + 0.0039$	0.10	0.30	0.9969	4.23	108.69

[a]Values determined for concentration 10 µg/mL ($n = 5$).

tailing due to hydrogen bonding was observed for aliphatic amines that further increased LOD values [37].

The RSD values, which are less than 5.64% for the majority of analytes at a concentration of 10 µg/mL ($n = 5$) indicate a good precision of DLLME–GC–NPD. In contrast, the RSD values for DLLME–GC–MS exceeded in some cases the allowed values due to LOD values being greater than 10 µg/mL. In both cases the recoveries were within the acceptable range and the linear range extended from LOQ to about 50 µg/mL.

Calibration parameters of the two procedures GC–NPD and GC–MS are compiled in Table 1 and Supporting Information Table S2, respectively.

Based on the calibration parameters, the procedure using DLLME–GC–NPD was selected for further analyses. The parameters that had a decisive influence on the selection of the procedure were substantially lower LOD and LOQ values.

3.3 | Application of the developed procedure to the analysis of real effluents

The developed procedure was applied to the determination of VNC content in raw effluents from the production of bitumens and in effluents subjected to various treatment processes. Identification of VNCs was based on retention times of individual analytes for which the confidence interval was taken ± 0.2% t_R [min].

TABLE 2 Concentrations of VNCs in raw effluents and in effluents treated with Oxone® reagent and hydrogen peroxide

No.	Compound	Concentration [µg/mL]				
		Raw effluent	Oxone®	Reduction (–) / increase (+) [%]	H_2O_2	Reduction (–)/ increase (+) [%]
1.	Pyridine	1.15 ± 0.11	0.911 ± 0.024	−20.78	0.361 ± 0.086	−68.61
2.	1-Nitropropane	0.581 ± 0.032	0.38 ± 0.019	−34.60	0.402 ± 0.013	−30.81
3.	Pyrrole	2.622 ± 0.061	2.881 ± 0.097	+9.88	<LOD	−≪99.99
4.	3-Methylpyridine	0.594 ± 0.012	0.492 ± 0.023	−17.17	0.142 ± 0.017	−76.09
5.	4-Methylpyridine	0.510 ± 0.011	0.562 ± 0.081	−10.20	0.151 ± 0.014	−70.39
6.	2,4-Dimethylpyridine	0.151 ± 0.011	0.173 ± 0.022	+14.57	<LOD	−≪99.99
7.	2,4,6-Trimethylpyridine	0.582 ± 0.023	<LOD	−≪99.99	<LOD	−≪99.99
8.	2-Ethyl-1-hexylamine	0.484 ± 0.034	(<LOQ ~ 0.124)	−~74.38	<LOD	−≪99.99
9.	Nitrobenzene	5.13 ± 0.23	<LOD	−≪99.99	<LOD	−≪99.99
10.	p-toluidine	10.86 ± .34	2.90 ± 0.26	−73.30	<LOD	−≪99.99
11.	2-Nitrotoluene	3.92 ± 0.17	<LOD	−≪99.99	<LOD	−≪99.99
12.	Quinoline	3.03 ± 0.22	7.40 ± 0.51	+144.22	7.07 ± 0.66	+133.33
13.	1,4-Dinitrobenzene	0.992 ± 0.077	(<LOQ ~ 0.452)	−~54.44	<LOD	−≪99.99
	X1	0.36	0.81	+125.00	0.28	−22.22
	X2	0.49	1.11	+126.53	0.87	+77.55
	X3	0.29	0.92	+217.24	0.51	+74.85
	X4	2.16	<LOD	−≪99.99	<LOD	−≪99.99
	X5	1.05	<LOD	−≪99.99	<LOD	−≪99.99
	X6	0.57	0.46	−18.44	0.28	−50.06
	X7	0.47	<LOD	−≪99.99	<LOD	−≪99.99
	X8	0.39	0.50	+27.81	<LOD	−≪99.99
	X9	3.09	<LOD	−≪99.99	<LOD	−≪99.99
	X10	<LOD	0.99	+100	<LOD	−≪99.99
	Sum of remaining unidentified VNCs	13.15	11.17	–15.02	2.55	–80.56
	Total VNCs	52.62	31.25	−40.62	12.62	−76.01

A total of 13 analytes were detected in samples of raw effluents at concentrations ranging from 0.15 to 10.81 µg/mL, with *p*-toluidine having the highest concentration followed by nitrobenzene (5.13 µg/mL), 2-nitrotoluene (3.92 µg/mL), quinoline (3.03 µg/mL), and pyrrole (2.62 µg/mL). In addition, a number of pyridine derivatives were identified at concentrations not exceeding 0.59 µg/mL. The occurrence of aromatic organonitrogen compounds in effluents from the production of bitumens is caused by side reactions taking place during vacuum distillation and oxidation of bitumens. In both cases thermal cracking occurs that leads to decomposition of high-molecular-weight nitrogen-containing organic compounds yielding derivatives of pyridine, pyrrole, and quinoline. Amines formed during cracking undergo partial oxidation with the formation of nitro derivatives. The nitro group can also be formed by addition of oxygen to heterocyclic compounds at the C–N–C site. In effluent samples treated chemically with hydrogen peroxide (H_2O_2), complete or partial reduction in concentration of all the identified analytes was observed except for quinoline whose concentration increased by 133.33%. An increase in concentration of quinoline as well as pyrrole, 4-methylpyridine and 2,4-dimethylpyridine was also observed in effluents treated with Oxone® reagent. In addition, concentrations of ten unidentified analytes having the largest peak areas were estimated (X1–X10 in Fig. 1). These concentrations were calculated from the calibration curve for pyridine. In effluent samples treated with hydrogen peroxide the majority of these unidentified analytes had reduced concentrations except for X2 and X3 whose concentrations increased by 77.55 and 74.85%, respectively. On the other hand, in effluent samples treated with Oxone® reagent an increase in concentrations of X1, X2, and X3 was observed as well as an appearance of a peak X10, which was originally absent from raw effluents. The remaining compounds underwent reduction in concentration that indicates only partial effectiveness of Oxone®

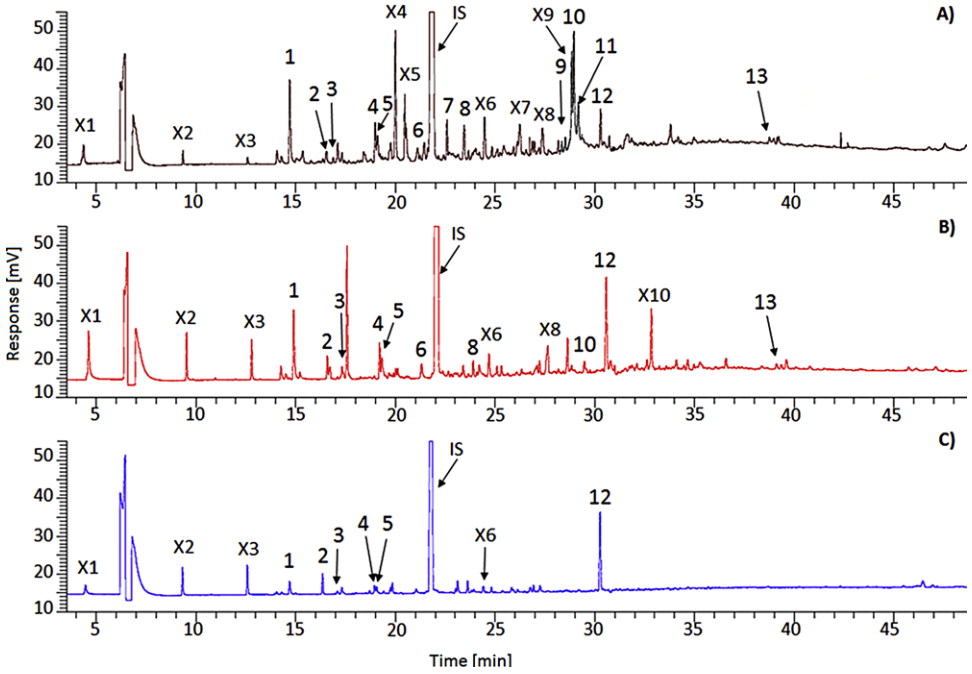

FIGURE 1 Chromatograms of postoxidative effluents (DLLME–GC–NPD). (A) Raw effluent, (B) effluent treated with H_2O_2, (C) effluent treated with Oxone® reagent. Peak numbers correspond to compounds from Table 2

and H_2O_2 in treatment of this type of effluent and the formation of secondary pollutants through oxidation of some groups of compounds. A comparison of total effectiveness of reduction in concentration of all organonitrogen compounds reveals a greater effectiveness of hydrogen peroxide compared to Oxone® reagent, for which the reduction in total VNC content was equal to 76.01 and 40.62%, respectively.

A detailed comparison of the effectiveness of treatment methods and changes taking place in samples is presented in Table 2 and Fig. 1.

4 | CONCLUDING REMARKS

We describe a new procedure for the determination of volatile organonitrogen compounds at low concentration levels in effluents from the production of bitumens using dispersive liquid–liquid microextraction coupled with GC and two alternative detectors: nitrogen-phosphorus detector (GC–NPD) and mass spectrometer (GC–MS). The studies demonstrated that the DLLME–GC–NPD system is best suited for the determination of VNCs in industrial effluents.

To maximize extraction yield, optimization of DLLME was carried out. Basic analytical characteristics obtained for the 32 standards demonstrate applicability of the developed procedure to the determination of VNCs at trace levels.

A comparison of analytical characteristics of the two systems investigated: GC–MS and GC–NPD proves superiority of the GC–NPD system due to its higher sensitivity. However, despite satisfactory parameters of the procedure, the NPD detector has limited signal stability due to mechanism of detection that is based on the generation of cold plasma on a rubidium bead. The bead has to be activated at a high temperature and the properties of the detector remain stable for a dozen or so days. Thereafter, the activity (and sensitivity) begins to drop. Additionally, the decrease in sensitivity can be caused by contamination of the bead by the stationary phase bleed, formation of a coat of silica, loss of rubidium, or adsorption of moisture. All these phenomena result in a decrease of ionization efficiency and a gradual drop in sensitivity. Such a detector has to be reactivated often or the entire bead replaced. Fortunately, NPD beads are relatively inexpensive (*ca*. $300–400), and conditioning restoring the original sensitivity of the detector can be performed multiple times. Such problems are not observed with the mass spectrometer. However, due to the low sensitivity of MS toward VNCs, GC–NPD is a better choice despite all the problems with the NPD detector.

Diverse effects were observed in samples subjected to different oxidants. For Oxone® reagent only a partial reduction of concentration of the analytes took place with simultaneous formation of new organonitrogen compounds either absent from raw effluents or present at lower concentrations, some of which are highly toxic. In contrast, the use of hydrogen peroxide resulted in a decreased concentration of the majority of the analytes. The results obtained indicate the need for the determination of VNCs in raw as well as treated effluents.

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