DETERMINATION OF BTEX IN SURFACE AND GROUND WATERS AT CENTRO EXPERIMENTAL ARAMAR AREA

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ABSTRACT

The mixture of the monocyclic aromatic compounds benzene, toluene, ethylbenzene and xylene isomers is defined as BTEX. The presence of BTEX in the environment is regularly associated with petroleum and its byproducts leakages or industrial effluent discharge. BTEX may cause serious problems to human and animal health. Human exposure to these aromatic compounds can lead to eye and skin irritation, central nervous system weakening and bone marrow depression. According to World Health Organization (WHO) benzene can cause cancer development. A new unit process in Centro Experimental Aramar (CEA) using BTEX-containing products will be launched shortly. Therefore, BTEX monitoring will be necessary since effluents release in Brazil is controlled by CONAMA regulations. Besides, as these compounds has never been evaluated in CEA, it is important to provide knowledge on the current BTEX concentration, in order to stablish pre-operational values in CEA region and nearby. The CONAMA regulations for BTEX in superficial waters sets very low limits (such as 0,002 mg L-1 for toluene and 0,005 mg L-1 for benzene). For this reason, it was developed in this work an analytical method by Headspace–GC-MS to achieve these values. The figures of merit determined were limit of detection (LOD), limit of quantification (LOQ), precision and accuracy. BTEX was analyzed in superficial waters from three different sampling points at Ipanema River and ground water collected in eight different sampling points. All sampling points were located a ratio 10 km radius from CEA.

1. INTRODUCTION

Water is a vital natural resource to human life and the environment. Although Earth is constituted of 70% of water, 97.5% of this amount is saline waters and only 2.5% is fresh water. Life depends on fresh water, which can not be substituted by anything else[1]. Anthropogenic activities can cause pollution problems, which must be controlled to guarantee human consumption of this hydric resource. Brazilian laws have become rigid, by setting maximum limits to several organic and inorganic contaminants in order to avoid the degradation of rivers and ground waters. In an effort to comply with these regulations, it is important to monitor the concentration of contaminants in natural water to assure they are at the established limits. The group of organic contaminants defined as BTEX (benzene, toluene, ethylbenzene and xylene isomers) are pollutant substances commonly found in these waters and are the aim of this work. Brazilian regulations that set limits to natural water are: Portaria 2914/2011 from Healthy Ministry for drinking water[2], CONAMA 357/2005[3] for surface waters and CONAMA 396/2008 for groundwater[4].CONAMA 357/2005 sets the most restrictive maximum limits. They are showed in Table 1.

Table 1: Maximum values for BTEX according CONAMA 357/2005

Compound	Fresh Water Quality Classs I – (mg L^{-1})
Benzene	0.005
Ethylbenzene	0.090
Toluene	0.002
Xylene	0.300

Petroleum and its byproducts leakages and industrial effluent discharge are contamination sources of BTEX [5]. Industries or production units using petroleum derivatives can produce effluents with light hydrocarbons, which are characterized by higher solubility in water.

Among these contaminants, BTEX is a cause for concern because they are toxic for humans and animals, affecting the central nervous system. They present chronical toxicity even in small concentrations. Benzene contamination is particularly worrying, because it is carcinogenic and mutagenic.[6-9]

The Centro Tecnológico da Marinha em São Paulo (CTMSP) is a research center whose goals are the development of the nuclear fuel cycle for energetic purposes and the nuclear submarine propulsion system. Its office is located at São Paulo University and the Experimental branch, called Centro Experimental Aramar (CEA) is located at Iperó in São Paulo State[10,11]. Since the Ipanema river, which belongs to Sorocaba river watershed,[12] cross through east-southeast of CEA three sample points were selected for this work, one before, one inside and one after CEA. The environmental sampling locations are showed in Figures 1A and 1B.
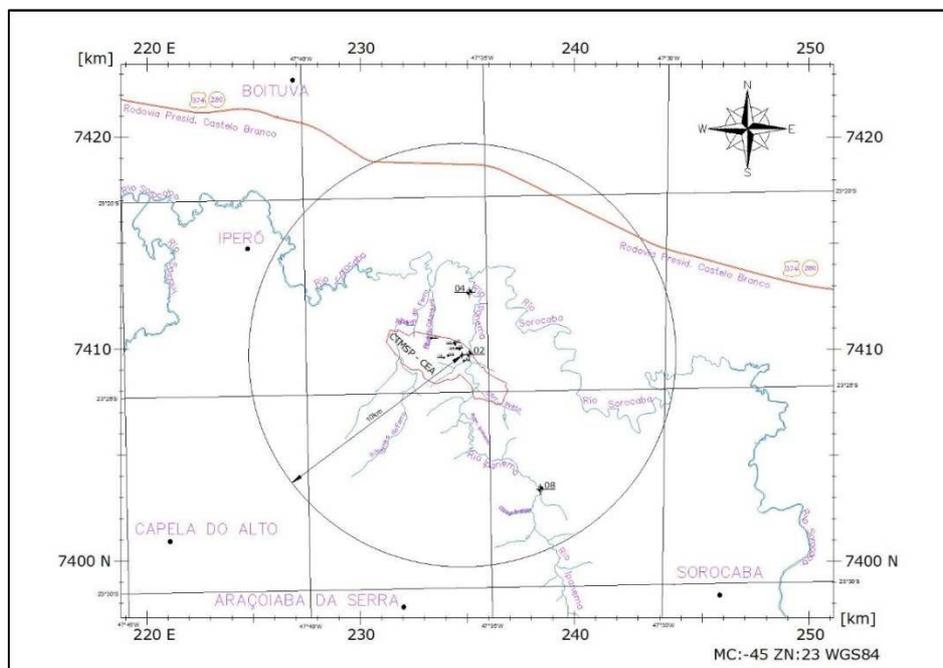

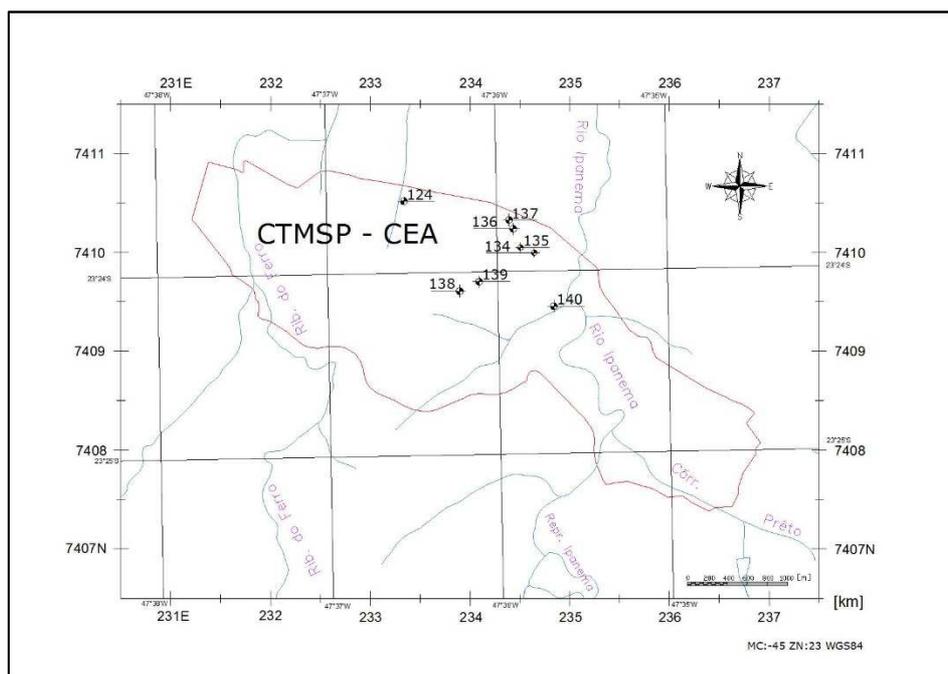**Figure 1A: Sampling locations (general view)**

Figure 1B: Sampling location of ground water

In CEA exists a superficial aquifer and according to the composition both surface water and ground water can be classified as bicarbonated calcic and sodic [13] with the main water flow driving to Ipanema river [12]. It were selected 9 sample points in order to evaluate the presence of BTEX in ground water, as shown in Figure 2.

A new unit process in Centro Experimental Aramar (CEA) using BTEX-containing products will be launched shortly. Therefore, BTEX monitoring will be necessary since effluents release in Brazil is controlled by CONAMA regulations. Besides that, as these compounds has never been evaluated in CEA, it was important to provide knowledge on the current BTEX concentration, in order to stablish pre-operational values in CEA region and nearby.

2. MATERIALS AND METHODS

2.1. Sampling locations

Table 2 shows the identification and water type (ground water or superficial water) for samples as well as the coordinates for the sampling locations.

Table 2: Sampling locations identification

Sample Identification	Type	Coordinates UTM (km)
AS02	Ipanema river	235.051E, 7409.710N
AS04	Ipanema river	235.290E, 7412.106N
AS08	Ipanema river	238.303E, 7403.542N

AP124	Groundwater	233.352E. 7410.483N
AP134	Groundwater	234.642E, 7409.993N
AP135	Groundwater	234.506E, 7410.045N
AP136	Groundwater	234.432E, 7410,234N
AP137	Groundwater	234.392E, 7410,324N
AP138	Groundwater	233.897E, 7409.603N
AP139	Groundwater	234.091E, 7409.699N
AP140	Groundwater	234.840E, 7409.453N

2.2 Analytical technique

BTEX determination is carried out by gas chromatography with mass detector (GC-MS). It was necessary to use pre-concentration techniques, such as headspace for achieving detection limits required by Brazilian regulations [5,6,14].

2.3 Equipment and reagents

All the measurements were made with Shimadzu CG-2010 Plus / GCMS-QP 2010 Ultra with autosampler AOC-5000 Plus using Headspace extraction.

Pure helium (99.996%) and BTEX Mix 2000 $\mu g.mL^{-1}$ in methanol SUPELCO were used in this work. BTEX Standard solutions were prepared by dilution from a stock solution in deionized water (MilliQ system,18.2 MΩ cm).

2.3.1. Chromatographic conditions [16]

Chromatographic conditions were tested aiming the best peak resolution. It was applied a column Rtx-5MS® from Restek® (30m x 0.25 mm x 0.25μm) and a 3.5 mm internal diameter straight inlet liner with 95 mm lenght. The column oven temperature program was: 35°C for 10 minutes, increasing temperature rate by 15°C min^{-1} until 120°C for 2 minutes. The injection temperature was 250°C, the split ratio was 20 and the column flow was 1 mL min^{-1}. A 1000μL gaseous sample from headspace was injected after 15 minutes kept at 80°C.

2.3.2 Mass spectrometer conditions

It was used an electron ionization source (EI-70 eV) with a mass analyser quadrupole. The ion source and interface temperature applied was 250°C.

3. RESULTS

3.1. Method Development

3.1.1. Expected Peak elution order

The chromatography column Rtx-5MS® from Restek® is a low-bleed GC-MS Columns (fused silica) with low-polarity phase; crossbond diphenyl dimethyl polysiloxane. Thus the separation order of the expected compounds should follow the boiling point sequence, as shown in Table 3. The chromatogram obtained from 0.1 mg L^{-1} BTEX standard applying SCAN-TIC mode was shown in Figure 2.

Table 3: Elution order, based on boiling points compounds [15]

Order	Compound	Boiling point (°C)
Peak 1	Benzene	80.1
Peak 2	Toluene	110.6
Peak 3	Etilbenzene	136.2
Peak 4	p-xilene	138.3
Peak 5	m-xilene	139.3
Peak 6	o-xilene	144.4

The mass spectra of all the ions present in each eluted peak are obtained continuously at fixed and determined times (Time Event condition in the MS parameters) in SCAN mode. In this way, the qualitative information of the compounds present in the sample can be obtained. The chromatogram obtained is the TIC (Total Ion Chromatogram) and represents the sum of the intensities of all the ions in a given retention time. The TIC chromatogram is similar to that obtained with an FID detector (Flame Ionization Detector) in gas chromatography
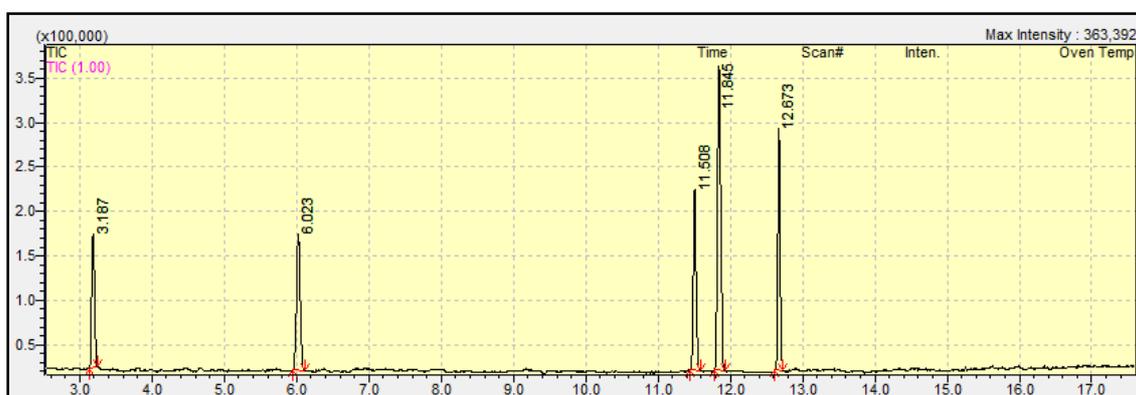

Figure 2: BTEX standard chromatogram (0.1 mg L-^{1}) SCAN-TIC mode

The obtained chromatogram presented five peaks for six compounds. Literature search, using the same stationary phase (95% dimethylpolysiloxane, 5% phenyl), showed that the co-elution of meta and para-xylene isomers occurs at the same peak, due to the low difference between boiling points for these two compounds (see Table 2). This is not a problem because in this work we are interested in the xylene isomers sum.

3.1.2. Mass Spectrum Identification

In the mass spectrum, the peak with the highest m/z (mass to charge ratio) represents the molecular ion and the base peak is the highest peak, since it has the highest abundance and receives a relative intensity of 100. Peaks with smaller m/z values are called fragment peaks and represent positively charged fragments of the molecule. As the molecular ion has the same molecule mass, since the electron mass is negligible [17], the expected m/z are shown in Table 4.

Table 4: Expected ion molecular mass for BTEX compounds

Compound	Molecular Formula	Ion Molecular mass
Benzene	C_6H_6	78
Toluene	C_7H_8	92
Ethylbenzene	C_8H_{10}	106
Xylene	C_8H_{10}	106

Since the same compounds yields the same fragments when using the same fragmentation energy (70eV), it was possible to use a NIST library software to identify and confirm the peak elution order. The mass spectrum of all peaks were compared with those ones from NIST library (Figures 3 to 7). Table 5 shows the confirmed peak elution order with the target ion chosen for SIM quantitative analysis.
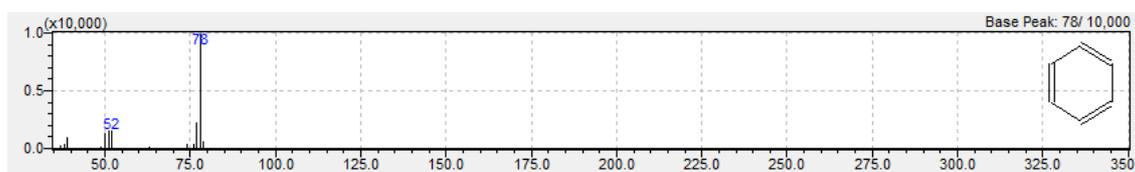

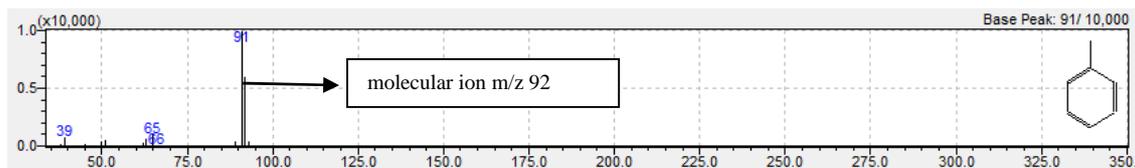**Figure 3: Benzene mass spectrum**
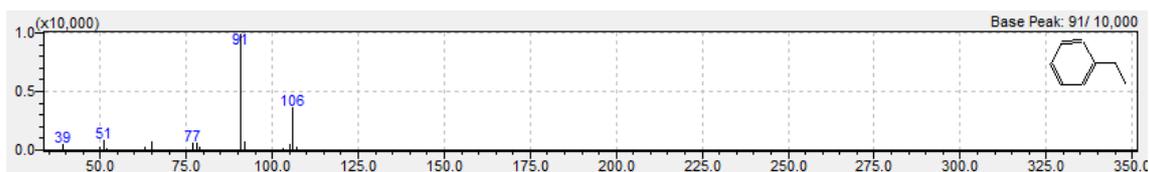

Figure 4: Tolune mass spectrum
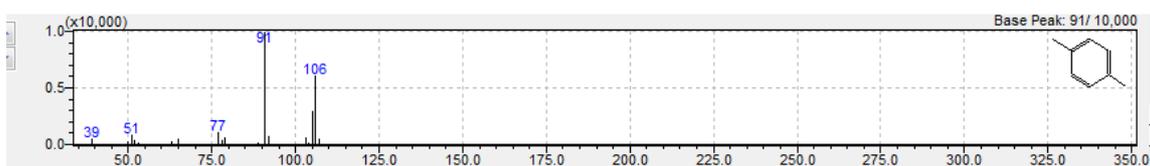
Figure 5: Ethylbenzene mass spectrum

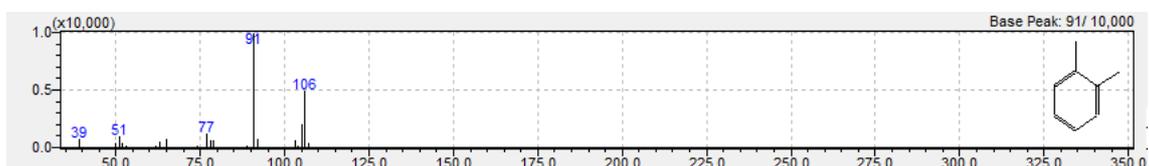**Figure 6: p-Xylene mass spectrum**

Figura 7: o-Xylene mass spectrum

Table 5: Peak Elution order, retention time and target ion for BTEX compounds

Peak	Compound	Retention Time (min)	Target
1	Benzene	3.187	78
2	Toluene	6.023	91
3	Ethylbenzene	11.508	91
4	*p-m*-Xylene	11.845	91
5	*o*-Xylene	12.673	91

3.2. Linearity

For natural waters (surface and ground waters) it was tested two analytical curves. One curve had the concentrations set close to regulations limits (CONAMA): 0.001, 0.002, 0.003, 0.004 and 0.005 mg L^{-1}. The other one had the concentrations a little higher: 0.002, 0.005, 0.010, 0.050 e 0.100 mg L^{-1}. In both curves was applied external standardization. As p-xylene and m-xylene elute in the same peak their concentration are added. The curves were obtained from the equipment software and the correlation coefficients (R^2) are shown in Table 6.

Table 6: Correlation coeficient (R^2)

Compound	R^2 Higher concentration curve	R^2 Lower concentration curve
Benzene	0,998	0,996
Toluene	0,999	0,997
Ethylbenzene	0,999	0,995
p-m-Xylene	0,999	0,996
o-Xylene	0,999	0,996

The curve with higher concentration showed better R^2 values, but in both cases, the results attended the criteria of $R^2 \geq 0,995$. Heleno et al. [5] showed values range 0.996 – 0.998 and Menghini et al [14] showed value range 0.997 – 0.998.

The normality analysis of residuals (difference between the obtained concentration and linear regression calculated concentration) was performed using Minitab software. The results showed that data follow normal distribution.

3.3. Limits of Detection and Quantification

The limits of detection (LOD) and quantification (LOQ) were determined by a series of analyses (8 replicates) of blank. LOD was calculated according to equation 1 and LOQ was calculated as ten times the LOD value. Table 7 shows the results.

$$LOD = X_{mean} + t_{student} * s \qquad (1)$$

where:
X_{mean} = medium results for blank
$t_{student}$ = value with 99% reliability and the number of degrees of 7
s = standard deviation of 8 replicates.

Table 7: Limits of Detection and Quantification

Replicate	Benzene (mg L^{-1})	Toluene (mg L^{-1})	Ethylbenzene (mg L^{-1})	m,p-Xylene (mg L^{-1})	o-Xylene (mg L^{-1})
1	0.00005	0.00014	0.00001	0.00002	0.00001
2	0.00000	0.00012	0.00001	0.00001	0.00001
3	0.00001	0.00012	0.00000	0.00001	0.00000
4	0.00010	0.00011	0.00001	0.00001	0.00001
5	0.00000	0.00012	0.00000	0.00001	0.00001
6	0.00000	0.00010	0.00001	0.00001	0.00001
7	0.00002	0.00013	0.00000	0.00001	0.00001
8	0.00000	0.00010	0.00000	0.00000	0.00000

Mean	0.000023	0.000118	0.000005	0.000010	0.000008
Standard Deviation	0.000036	0.000014	0.000005	0.000005	0.000005
LOD	**0.0001**	**0.0002**	**0.00002**	**0.00003**	**0.00002**

In order to apply the same LOD for all compounds the worst scenario was used: 0.0002 mg L^{-1}. The LOQ in this is case is 0.002 mg L^{-1}. This value was set as the first point of analytical curve with higher concentration.

The LOD was verified with a 0.0002 mg L^{-1} standard. The obtained chromatogram is showed in Figure 8.
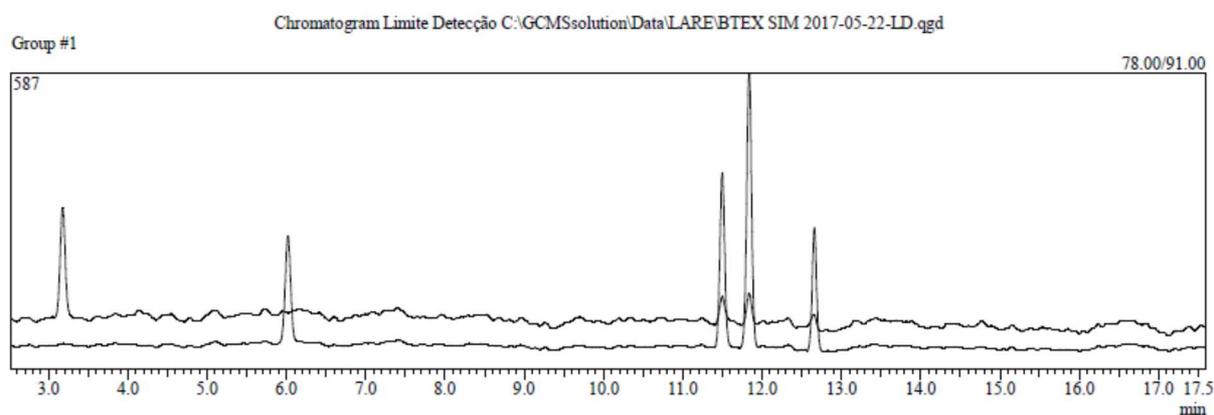

Figure 8: BTEX LOD chromatogram (0.0002 mg L-^{1}) SIM mode

3.4. Precision

In order to evaluate the precision seven 0.002 mg L^{-1} standards were analyzed. The precision, expressed as a relative standard deviation (RSD, seven replicates) was 11% for benzene, 12% for toluene, 11% for etilbenzene, 10% for *meta* and *para* Xilene isomer and 9% for *ortho*-Xilene

3.5. Accuracy

The accuracy of the proposed methodology was evaluated by means of spiked samples in three different concentrations as showed in Table 8. The concentrations of all samples before the standard addition was below of LOD.

Table 8: Recoveries of spiked samples

Sample	Spiked concentration (mg L^{-1})	Recovery (%) Benzene	Recovery (%) Toluene	Recovery (%) Etilbenzene	Recovery (%) m-p-Xilene	Recovery (%) o-Xilene
AP134	0.002	98.0	93.5	87.0	85.5	89.0
AP135	0.002	89.0	87.0	85.5	85.0	88.5
AP136	0.002	91.0	89.0	85.5	85.3	88.0
AP137	0.005	87.4	84.6	81.8	83.2	85.8
AP138	0.005	83.0	82.0	79.6	80.6	83.4
AP139	0.005	83.6	81.0	78.6	79.9	82.8
AS02	0.010	74.7	76.3	74.0	73.6	75.3
AS04	0.010	73.0	72.7	68.5	67.9	70.6
AS08	0.010	61.9	65.9	64.7	64.2	66.8

According to AOAC [18] the expected recovery as a function of the analyte concentration is 40-120% for 0.001 mg L^{-1} and 60-115% for 0.010 mg L^{-1}. All recoveries obtained lies entirely within the allowed ranges.

3.6. Results for superficial water from Ipanema River and ground water from CEA area

The superficial waters were evaluated in three samples collected at Ipanema River accordingly to Table 1.

The results for BTEX compounds at samples AS02, AS04 and AS08 from Ipanema River (September/2016 to April/2017) showed results below LOQ.

The ground water from CEA area is collected every six months. Due to this sampling interval, the analyses were carried out twice.

All the results for BTEX compounds at samples AP124, AP134, AP135, AP136, AP137, AP138, AP139 and AP140 were below LOQ.

3. CONCLUSIONS

The proposed method proved to be effective for BTEX determination with good linearity ($R^2>0.99$) for all compounds, precision expressed as RSD between 9-12% and accuracy of all spiked samples within the allowed range.

The evaluation of superficial and ground waters showed results below LOQ as well as CONAMA maximum limits for all compounds in samples for CEA influence area.

The importance of this work was to collect chemical information from CEA surroundings to start a database of these compounds before the CEA's new unit process using BTEX-containing products initiates its activities.

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