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Analytical Methods

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TECHNICAL NOTE

An improved method for BTEX extraction from charcoal

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Abstract In this paper we propose a simple procedure for the extraction of BTEX (benzene, toluene, ethylbenzene and xylenes) from activated charcoal. For this purpose synthetic samples were prepared in laboratory and real samples were collected in a polluted environment using passive sampling. The proposed extraction procedure is based on the use of an appositely designed soxhlet apparatus which dimensions are as small as the cartridge of the passive samplers, in order to accommodate this latter and permit to use a small amount of solvent. The selection of solvent was based on the strong request to substitute carbon disulfide, which is by far the solvent of choice, with less hazardous substance in order to enhance operator protection. Among the solvents tested the best results were found by using dichloromethane that, under optimized conditions, led to a complete recovery (>97%) of each analyte (BTEX), both in the synthetic and the real samples. The extracting procedure, with CH_2Cl_2 in the soxhlet last about 20 minutes which also results in a reduced operating time.

Introduction

Aromatic hydrocarbons, such as benzene, toluene, ethylbenzene and xylenes (commonly called BTEX) are widely present in the environment. These compounds can be generally found in gaseous phase and have a key role in the chemistry of the troposphere [1,2]. Major sources of aromatics to the urban environment include vehicle exhaust (mobile sources), petroleum refining processes, residential heating, waste incineration, coke ,aluminium production (stationary sources) and gas fuel stations [3,4,5]. The presence of BTEX in the urban atmosphere has a direct impact on human health because of their carcinogenic and mutagenic potential [6], therefore they need to be monitored periodically. The techniques used for BTEX monitoring are usually based on their sorption in a tube (active or passive devices) which is filled with a suitable sorbing agent, usually activated charcoal, followed by solvent desorption with CS_2 and gas chromatographic determination [7,8]. In Italy, at the best of our knowledge, more than 95% of laboratories of environmental analysis follows this procedure notwithstanding alternative techniques are well known but not commonly used, among the others, thermal desorption and accelerated solvent extraction [9], because of their high costs.

Occupational carbon disulfide exposure has been associated with a variety of health effects stimulating some epidemiological researchers to study the potential relationships between the exposures and neurological, reproductive, cardiovascular or endocrine dysfunctions as well as eye and skin irritations. It has been reported that CS_2 induces diffuse vascular encephalopathy, parkinsonism and peripheral polyneuropathy [10,11,12]. The US Occupational Safety and Health Administration (OSHA) indicates for CS_2 12.4 mg/m^3 as an 8-h TWA concentration [9]. However Godderis et al. [13] demonstrated that diminished neurobehavioral functions in workers currently exposed to CS_2 could be detected even if average exposure was as low as ≤ 10 mg/m^3 in a relatively short time (<10 years exposure). Therefore they concluded that the current TLV insufficiently protects against neurological effects and should be lowered.

The request to find less hazardous substituted was first caught by Bertoni and Ciuchini [14], who investigated on the feasibility of substituting CS_2 in the desorption of COV sampled on activated charcoal adsorbents, with dichloromethane. CH_2Cl_2 is a good solvent for GC analysis because it has a low boiling point and it doesn't interfere with other analytes, it has an higher TLV (174 mg/m^3) and is less expensive with respect to CS_2. The results of BTEX extraction

with CH_2Cl_2 were not satisfying because the recovery ranged from 90% for benzene to 55% for o–xylene. They also tested different solvents to increase the recovery, without achieving appreciable results.

This study follows and completes the investigations of Bertoni and Ciuchini with particular attention to BTEX extraction from passive devices filled with activated charcoal. We screened a large number of solvents and CH_2Cl_2 turned out to be the most efficient in our experimental conditions.

Moreover, CH_2Cl_2 is already used in ultrasonic extraction procedures for BTEX, as recommended by EPA standards [3,4,5]; this procedure is, in fact, a valid alternative to the employment of CS_2, though many laboratories still prefer Soxhlet extraction for its simplicity and low cost of the basic equipment [15].

We performed the extraction of BTEX with CH_2Cl_2 by using a small Soxhlet appositely designed to contain the cartridges of the passive samplers. Recently Soxhlet has been defined as a "panacea" in the field of extraction [15], where the development of new technologies has improved its performance opening the door to the utilization in a number of different approaches. Optimizing the extraction procedure we obtained quantitative recoveries for each analyte after only eight extraction cycles, that last about 20 minutes. Moreover we applied the same procedure to analyze real environmental samples and found data comparable to CS_2 extraction in all cases.

Experimental

Reagents

The organic solvents used to desorb BTEX from activated charcoal were pentane, isopropanol, acetonitrile, dichloromethane, carbon disulfide, diethylether, chloroform and methylethylketone. Stock standards in all solvents were prepared from benzene, toluene, ethylbenzene and o-, m-, p-xylenes. The solutions were kept at 4 °C. All reagents were purchased from Sigma Aldrich at reagent grades and used without any purification. Carbon disulfide was bought form Sigma Aldrich, declared as product with low benzene contamination.

Samplers and field sampling

RING passive samplers filled with activated charcoal (300 mg) were obtained from Aquaria Research srl, Italy.

Field sampling was conducted in the city of Salerno (Italy). The measurement site was a commercial area characterized by an elevated traffic density. Each sampler was exposed for 72 h, at a height of approximately 2 m above the street level. Average temperatures were measured by a thermometer data-logger with ± 1.0°C accuracy. For each sampling two samplers were exposed and, after the sampling, they were transported and stored at less than 4°C until analysis and were processed within a week after their arrival in the laboratory.

Chromatographic conditions

Analysis was done by a GC-FID (Agilent 7890A) equipped with HP-5 column (50 m×0.2 mm id, 0.25μm). GC oven was programmed to 60 °C, 2-min hold, ramped to 140°C at a rate of 6°C/min following a 2-min hold, then ramped to 250 °C at a rate of 20 °C/min following a 10-min hold. Helium was used as carrier gas with a flow rate of 1 mL min^{-1} and splitless injection mode was used. The injection volume was 1 μL. It has to be underlined that in these experimental conditions, the peak of

benzene is well separated from that of the solvent and easily integrable.

Results

Apparatus description and extraction conditions

Preliminary tests were performed on laboratory prepared samples in order to compare the extraction capacity of selected solvents with carbon disulfide. Synthetic samples were prepared by injecting 1.0 μL of each compound (benzene, toluene, ethyl-benzene, o-xylene, m-xylene and p-xylene) to 10 g of activated charcoal into a closed chamber. The system was kept closed for 24 hours and charcoal was finally removed and maintained under N_2 atmosphere before analysis. Analyses were conducted on 300.0 mg of sample, i.e. the same amount as in a RING passive sampler, which contains 2.65 μg benzene and xylenes and 2.63 μg of toluene and ethyl-benzene. Classic extraction with CS_2 was performed by desorbing the analytes directly into a glass tube for about 30 minutes with 2 mL of solvent (CS_2, low benzene, Sigma Aldrich) following NIOSH method 1501 [8], than the extract was filtered on cellulose based filter to remove carbon residues and successively injected for the gas chromatographic analysis. The same procedure was followed for the other solvents; samples were extracted by using 2 mL of solvent for 30 minutes in a closed glass tube and successively analyzed by GC-FID. The blank was prepared by using activated charcoal without any treatment.

Figure 1 shows the performances of the various solvents tested, where the extraction capacity of each solvent was normalized with respect to the extraction capacity of CS_2 (100%). Dichloromethane resulted to give the best results with an efficiency of about 80% with respect to CS_2. Since CH_2Cl_2 is also suitable for gas chromatographic analysis (low boiling point and poor response to FID), we used it to test our proposed extraction procedure.
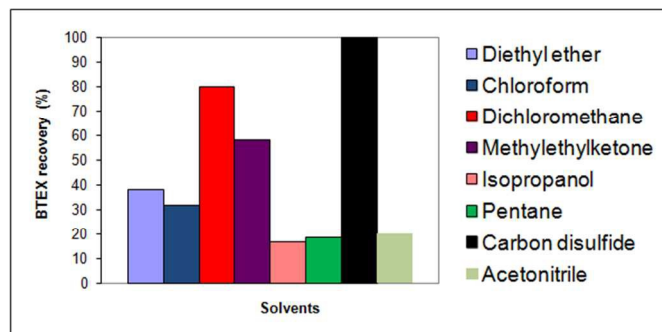

Figure 1. BTEX recovery (%) (average of the average of three replicates) with different solvents.

300.0 mg of contaminated charcoal were introduced into the steel cartridges of passive samplers; the BTEX were successively extracted by using a specifically designed mini-soxhlet apparatus (Microglass Heim s.r.l., Italy. Figure 2), in order to enhance the extractive capacities of the solvent. The steel cartridges were employed to eliminate possible losses of carbon from the siphon to the solvent reservoir. The soxhlet extraction chamber was dimensioned to fit the passive sampler cartridge (2 cm i.d. × 4 cm height) and to guarantee a complete contact between solvent and substrate. 10 mL of solvent were used for each extraction, after which samples were collected in a volumetric flask and, in case of CH_2Cl_2 loss, fresh solvent was added up to 10 mL before analysis.
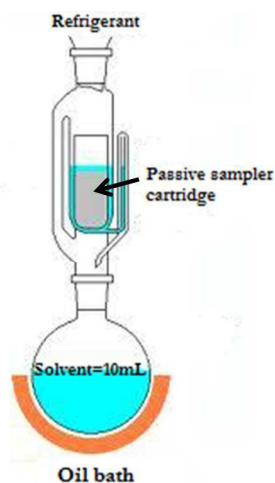
Figure 2. Soxhlet apparatus for BTEX (extraction chamber 2cm i.d. × 4 cm height, passive sampler cartridge 0,9 cm i.d × 3,3 cm height, bottom flask volume 20 mL).
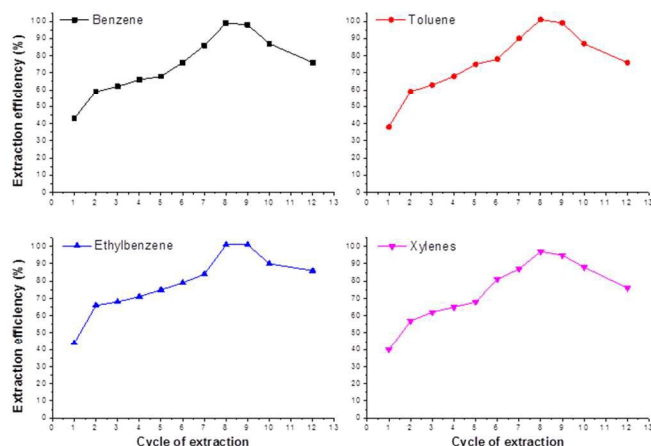

Figure 3. Extraction efficiency (%) vs number of cycles for BTEX using soxhlet apparatus.

Figure 3 shows that the maximum recovery for BTEX compounds was obtained after eight cycles of extraction (~ 20 minutes), whereas 80% of the recovery was obtained with 5/6 cycles. After eight cycles a decrease in the extraction efficiency was observed due to possible losses from soxhlet apparatus [16]. The bath temperature was adjusted to 80°C to guarantee a rapid and effective extraction. As shown in Table 1 quantitative recoveries for BTEX compounds were obtained. The relative standard deviation of eight replicate was lower than 4% in all cases.

Table 1. Recovery after eight cycles of extraction in soxhlet by using CH_2Cl_2.

Compound	Recovery (%)
Benzene	99 ± 3
Toluene	100 ± 4
Ethylbenzene	100 ± 2
Xylenes	97 ± 3

Passive sampling and field measurement

After laboratory tests with synthetic samples, the soxhlet extraction procedure was successively applied for the BTEX extraction from passive samplers exposed in a high-traffic street. Radial diffusive sampler was first invented in 1990 by Eickeler and Löffenholz [17] as a dosimeter for detecting gases or aerosol. This tool is very useful for monitoring many classes of substances such as VOCs, nitrous and sulfuric oxides, ammonia, volatile acids and, more recently, carbon dioxide [18,19].

Diffusive cartridges having a radial symmetry for a high sampling rate, have been employed for monitoring common pollutants concentration in atmosphere [19,20] and particularly BTEX [21,22], the most common among the volatile organic compounds generally present in a polluted environment. Radial symmetry provides higher sampling rates than other types of passive samplers.

This passive sampler consists of an adsorbent cartridge packed with 300 mg of activated charcoal inserted in a microporous polyethylene membrane. The compounds diffuse through the membrane toward the cartridge driven by the gradient of concentration between the ambient air and the inner cartridge. Compound concentrations C (mg/m^3) can be calculated by applying an equation derived from Fick's first law of diffusion:

$$C\left(\frac{mg}{m^3}\right) = \frac{m_d - m_b (mg)}{10^{-6} \times P\left(\frac{mL}{min}\right) \times t(min)}$$

Where m_d is the adsorbed mass of the analyte sampled during the time t while m_b is the mass of the analyte on a non-exposed cartridge (blank), P is the diffusive uptake rate of the substances (73 mL/min for benzene, 66 mL/min for toluene, 60 mL/min for ethylbenzene, 58 mL/min for o-xylene and 64 mL/min for m&p-xylenes), supplied by the Ring manufacturer. BTEX monitoring was carried out in Salerno (Italy), a medium sized town (138000 inhabitants over a 59 km^2 area). The measurement site was a commercial area characterized by an elevated traffic density. Samplers (two for each measurement set) were exposed approximately at 2 m above the street level for 72 h. After the sampling, they were transported and stored at less than 4°C until analysis and they were processed within a week after the arrival in the laboratory. Before analysis, charcoal contained in the two samplers was removed using an appropriate nipper, unified and successively divided again in two rates in order to eliminate any possible difference, than extracted concurrently using CH_2Cl_2 in the soxhlet apparatus and CS_2 by using the standard procedure. In Table 2 results for one month sampling campaign are summarized.

Recovery and detection limit (LOD)

According to EN 13528-2 the limit of detection (LOD) is expressed as three times the standard deviation of the blank values, while the limit of quantification (LOQ) is 10 times the standard deviation of the blank values. We calculated the LOD and LOQ values in $\mu g/m^3$ considering a 7 day sampling period at 25°C. The detection limit was 0.1 $\mu g/m^3$ for benzene, 0.05 $\mu g/m^3$ for toluene and 0.1 $\mu g/m^3$ for ethylbenzene and xylenes.

Table 2. BTEX concentrations in environmental samples.

Sampling	Benzene (µg/m³)		Toluene (µg/m³)		Ethylbenzene (µg/m³)		Xylenes (µg/m³)	
	CH_2Cl_2	CS_2	CH_2Cl_2	CS_2	CH_2Cl_2	CS_2	CH_2Cl_2	CS_2
1	4.5	4.3	9.2	9.3	1.9	2.0	14.0	13.7
2	11.9	11.8	21.2	21.0	3.9	3.7	27.0	27.3
3	10.3	10.6	25.7	25.8	3.4	3.6	21.9	21.7
4	0.4	0.3	1.0	1.1	0.3	0.5	1.8	1.7
5	9.6	9.8	16.6	16.4	2.2	2.0	19.1	19.2
6	6.3	6.2	15.3	15.1	2.2	2.1	17.4	17.2
7	0.7	0.5	0.9	1.0	0.4	0.3	2.5	2.3
8	1.2	1.0	2.0	1.8	0.4	0.4	3.8	3.7
9	7.5	7.5	15.5	15.3	2.3	2.1	15.4	15.2
10	2.3	2.1	6.3	6.0	0.9	0.7	6.5	6.3

Discussion and conclusions

The BTEX extraction from activated charcoal with CH_2Cl_2 in a soxhlet apparatus was optimized and compared with the standard CS_2 procedure. The results relative to synthetic samples are shown in Table 1. As can be seen, quantitative recoveries for the volatile BTEX compounds (benzene, toluene, ethylbenzene and xylene) were obtained. Moreover, the standard extraction with CS_2 actually extracts only 95% of the analyte during one extraction step and only after a second extraction step, in the same condition, the recovery is complete. In order to compare the performances of the soxhlet method with the standard, we treated the same samples (in duplicate) in the soxhlet with dichloromethane and with a two-step extraction procedure with CS_2. The results were the same and the recovery was complete (100%) for each analyte. The results we found show how soxhlet extraction using dichloromethane permits an excellent extraction compared to that of carbon disulfide. Respect to CS_2 procedure, our method requires a larger amount of solvent (10 mL CH_2Cl_2 *vs*. 2 mL CS_2), however soxhlet extraction could be simply associated with other technologies, such as microwave or high pressure assisted procedures, to improve the extraction time and reduce solvent volume [15]. The use of CH_2Cl_2 as extracting solvent instead of CS_2 is attractive and will result in a less hazardous procedure, thus eliminating the worker's exposure to carbon disulfide. Moreover, the performances of our method are comparable with those of the ultrasonic extraction procedure, showing also few advantages. The full procedure for the ultrasonic extraction requires about 90 minutes and involves some steps operated at low temperature to avoid analytes loss by volatilization [24]. In contrast, our method requires about 20 minutes, there is no need to operate at different temperatures other than the soxhlet one and no filtration or separation to remove the charcoal particles is required. Also, the extraction yield for more volatile compounds, such as Benzene, results significantly improved by using the soxhlet method respect to the ultrasonic procedure (98% *vs*. 63%) [24].
The CH_2Cl_2 soxhlet extraction was tested by analyzing real samples where BTEX were collected by exposing RING diffusive devices in a polluted environment in the city of Salerno, Italy. Results are showed in Table 2. Also in this case the recovery, compared to the extraction with CS_2, was complete, demonstrating an excellent potentiality of using passive sampling and soxhlet extraction with CH_2Cl_2 as a

solvent for the recovery of VOCs in studies of pollutants in the environments.
These results are comparable with some recently published data where the extraction of BTEX was performed with ASE instrumentation on environmental samples by using acetone or acetonitrile as solvents [9, 25].
Notwithstanding many advanced new techniques have been proposed in the last years for rapid extraction of COV, the classic Soxhlet [15] is however a simple and inexpensive tool that can encourages the substitution of carbon disulfide with less hazardous solvents.

Acknowledgements

Notes and references

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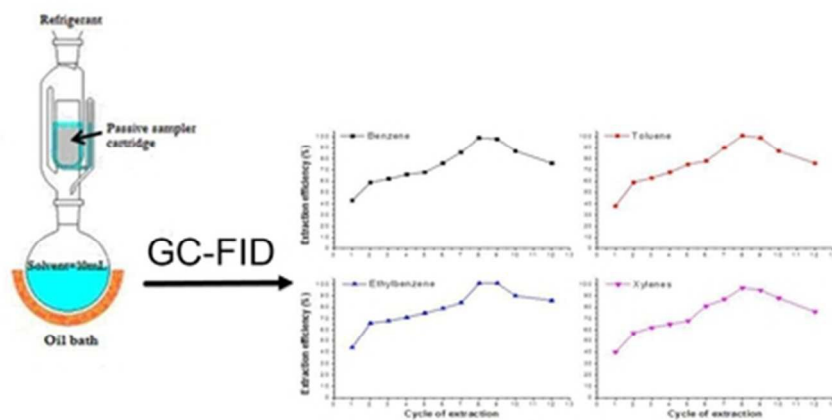
A mini-soxhlet for the efficient extraction of BTEX from charcoal using dichloromethane as alternative to CS2.
39x19mm (300 x 300 DPI)