

Selective extraction of benzoic acid from landfill leachate by solid-phase extraction and ion-exchange chromatography

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Abstract

In this work a simple method was described for selective extraction of benzoic acid from landfill leachate samples. The samples were submitted to solid-phase extraction (SPE) with XAD-4 resin as the stationary phase and ion-exchange chromatography (IEC) using the ion-exchange resin Amberlyst A-27. The instrumental analysis was performed by gas chromatography with mass spectrometric detection (GC-MSD). Benzoic acid was isolated, identified and quantified. The extraction process is rapid, simple and of low cost. It was also environmental friendly, that is, it was used a minimum amounts of hazardous organic solvents and produced also minimum quantities of residues.

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1. Introduction

Landfill leachate is a liquid formed by the degradation of the organic matter present in landfill. With the rain falls, this liquid that presents high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) can percolate the landfill and contaminate the soil, superficial and ground waters [1,2].

The leachate resulting from household wastes can be more toxic than the industrial waste leachate [3]. The greater toxicity levels are detected in sanitary landfills that received industrial residues mixed with household residues. To reach a concentration without toxic effects to all the species, the leachate samples landfills must be, sometimes, diluted by a factor higher than 10 000.

Many authors have worked in the identification and quantification of organic contaminant from landfill leachate [4,5]. Several substances with confirmed carcinogenic or

co-carcinogenic potential—dodecane, chloroform, carbon tetrachloride, benzene, toluene, xylene, phenol, chlorophenols, nitrophenols, anthracene and dichloromethane—were identified in landfill leachate [6]. Other substances, suspects of carcinogenic activity, as phthalate esters and bisphenol A, were also identified in landfill leachates [7,8].

Benzoic acid is used as a food preservative [9] and in the manufacture of various cosmetics, dyes, plastics, and insect repellents. It is very slightly soluble in water and highly soluble in organic matter. High bioaccumulation can be expected for this compound.

Short-term exposure to benzoic acid can irritate the eyes, the skin and the respiratory tract, and long-term or repeated exposure may cause skin sensitization [10]. Although, benzoic acid is not classifiable as carcinogen for humans and the available data on the carcinogenicity in animals are contradictory [11]. At this point, it is clear that more research about benzoic acid toxicity for human and animals has to be made and the monitoring of this compound in the environment must be a constant preoccupation. By this way, the investigation of the chemical composition of the landfill leachate and, specially, the presence of compounds that can be hazardous, like benzoic acid has gain more importance in the last years.

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However, isolation of pure fractions of organic compounds from landfill leachate is still difficult, time consumer and, sometimes, requires sophisticated equipment. Because this, there is a lack of works with this concern. This work describes a new application of SPE and IEC methods for selective extraction of benzoic acid from a complex matrix like landfill leachate. Benzoic acid identification, as well as the relative retention of this compound in XAD-4 and A-27 resins, was made by the GC–MS system library and comparison with chromatographic standard.

2. Experimental

All the solvents were analytical-reagent grade and distilled twice in glass apparatus. All the glass material was carefully washed with acetone, *n*-hexane and dichloromethane (DCM) and oven dried at 300 °C. Some chromatographic standard compounds were purchased from Aldrich.

The samples of landfill leachate were collected in a sanitary landfill located in Porto Alegre City, Rio Grande do Sul State, Brazil. This landfill receives, exclusively, municipal solid wastes. The samples were collected in glass bottles covered with an aluminum foil to prevent contamination. The samples were filtered at low pressure and maintained at 4 °C, protected of light, until the extraction procedures (no more than 24 h after the collection). The sample pH varies from 7 to 8 for all the samples, and they were used without any modification in this parameter.

The polymeric resins XAD-4 and A-27 were purchased from Merck and purified before use. The main resin characteristics are showed in Table 1.

The resins were activated according the following procedure: 10 g of the A-27 resin were mixed with a solution of NH₄OH (5 ml) and methanol (45 ml). The mixture was stirred for 3 min and after a few minutes in rest, it was washed with 25 ml of methanol, water (until pH 7), 25 ml of acetone and 25 ml of *n*-hexane. The XAD-4 resin was purified by soxhlet extraction with DCM during 4 h.

The samples were firstly submitted to SPE with a non-polar stationary phase (XAD-4) to avoid the presence of metal ions in the organic extract, which can prejudice the IEC extraction. The organic compounds stay adsorbed in the resin while the impurities cross the column and are loaded by the water (present in the sample).

The first step of the extraction was a clean up by passing through a glass column (15 cm × 11 mm i.d.) packed with 1 g of XAD-4 resin previously treated as described above. The stationary phase was washed with 10 ml of a methanol–acetone (3:7, v/v) mixture and 30 ml of distilled water.

Hundred milliliters of the sample was percolated through the column. After this, the column was dried under vacuum by 10 min and the analytes were extracted with 10 ml of the methanol–acetone mixture. This organic extract, after reducing the volume under a gentle flux of ultra-pure nitrogen until 5 ml, was added to a second column, with the same dimensions of the first, dry packed with 1 g of cationic exchange resin A-27. This column was then washed with 2 ml of *n*-hexane. The analytes concentrated in the column were eluted with 3 ml of a mixture of formic acid–diethyl ether (1:10, v/v). After volume reduction to 1 ml this extract was submitted to instrumental analysis. All the extraction procedures were made in triplicate.

An aqueous spike solution at 10 mg l⁻¹ was also submitted to SPE and IEC, in triplicate and at the same conditions that the real samples, to verifying the capability of the A-27 resin for retention of hydroxyl organic compounds and for a positive identification of the benzoic acid. After the volume reduction to 0.5 ml, an internal standard (biphenyl) was added to the extract eluted from the XAD-4 and the volume solution was elevated to 1 ml. The final concentration of the internal standard was 10 mg l⁻¹. The same procedures were adopted for extract eluted from the A-27 column.

As benzoic acid can be used for some plastics production, extraction blanks (distilled water) were made to ensure no contamination peaks caused by laboratory plastics materials.

Triplicate injection of 1 µl of the organic extracts from the XAD-4 and A-27 resin of the real samples and of the spike solution were made in a gas chromatograph–mass spectrometer Shimadzu QP5050A equipment. It was used the GC–MS in the electronic impact ionization mode at 70 eV. The column used was a HP-1 (polydimethylsiloxane) fused silica open tubular column, 25 m × 0.20 mm i.d., 0.11 µm film thickness. The temperature program was started at 70 °C, heated at 3 °C min⁻¹ to 200 °C, heated at 10 °C min⁻¹ to 280 °C and stayed at this temperature for 5 min. The split/splitless injector, in the split mode (1:50), was kept at 280 °C and the interface was kept at 280 °C. Helium was used as carrier gas at a flow rate of 1.0 ml min⁻¹. For quantitative purposes, GC–MS was used in the single

Table 1
Main stationary phases characteristics

Resin	AG	Maximum temperature	Area (m ² /g)	PV	EC
A-27	–N(Me) ₂ H ⁺ ·Cl ⁻	60 (OH) 80 (Cl)	65	51%	2.6 meq./g 0.7 meq./ml
XAD-4	–	–	725	20–60	0.98 ml/g

AG: active group; PV: porous volume/wet mesh size; EC: exchange capacity/pore volume.

ion monitoring (SIM) mode and the monitored ions were 59, 71, 74, 121 and 122.

3. Results and discussion

The chromatographic analysis of blanks did not show any peak, which indicates that no important interference exist in the process, including all the solvents and adsorbents.

Fig. 1 shows the monitored ion chromatogram (MIC) of the extracts obtained from elution of spike solutions through the columns packed with the resins XAD-4 (Fig. 1a) and Amberlyst A-27 (Fig. 1b). Fig. 2 shows the MIC of the extracts obtained from elution of real samples through the columns packed with the resins XAD-4 (Fig. 2a) and Amberlyst A-27 (Fig. 2b).

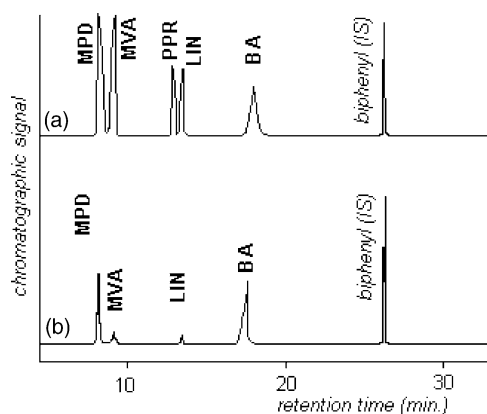


Fig. 1. Selective ion monitoring chromatogram of an aqueous spike solution with the six standard compounds at 10 mg l^{-1} , after the extraction procedures in the XAD-4 column (a) and the A-27 column (b). Chromatographic conditions are described in the text.

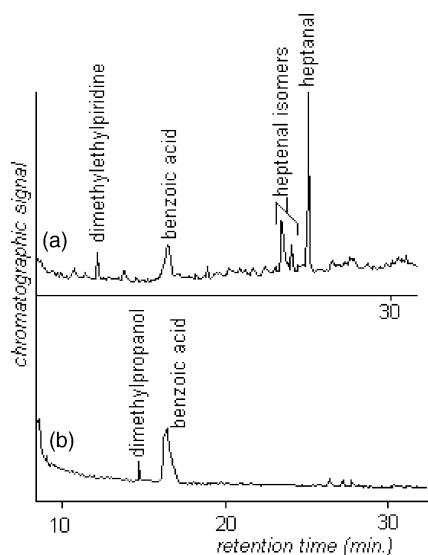


Fig. 2. Selective ion monitoring chromatogram of the extracts of a real sample of the XAD-4 column (a) and the A-27 column (b). Chromatographic conditions are described in the text.

Table 2

Relative retention of the standards compounds in XAD-4 and A-27 resins

Compound	M_r	Ion	Retention (%)	
			XAD-4	A-27
2-Methyl-2,4-pentanediol (MPD)	118	59	89.47	39.38
Methylvaleric acid (MVA)	116	74	95.47	1.30
2-Phenyl-2-propanol (PPR)	136	121	97.90	0.18
Linalool (LIN)	154	71	74.78	0.32
Benzoic acid (BA)	122	122	98.31	100

In these figures it is possible to see that the extract from the Amberlyst A-27 column shows a significant peak of benzoic acid. The relative average area of the benzoic acid peak in the A-27 extracts was of 42.9%. Considering that dry mass of the extracts was of 126 mg, the concentrations of benzoic acid in these extracts was around 540 mg l^{-1} . These results point out that the Amberlyst A-27 resin is very selective for benzoic acid extraction. This extreme selectivity of the Amberlyst A-27 stationary phase is confirmed by the chromatograms of the standards mixture submitted to same extraction procedures that the real samples (Fig. 1).

This behavior can be explained by the combination between the OH group of this compound and the exchangeable proton of the stationary phase. This combination results in water elimination and an effective positive charge on the carbonyl carbon, which acts, in this form, as a counter-ion of the stationary phase.

Table 2 shows the relative retention of the standards compounds in the XAD-4 and A-27 resins. It is considered that the relative area (area of the compound divided by the area of the internal standard, biphenyl) of each compound in the standard solution without suffering any extraction procedure, it corresponds to 100%. The percent of retention of each compound in the resin XAD-4 corresponds to the division of the relative area of the compound in the solution after the pre-concentration procedures in this resin, by the relative area in the previous standard solution, multiplied by 100. The percent of retention of each compound in the resin A-27 corresponds to the division of the relative area of the compound in the solution after the pre-concentration procedures in this resin for the relative area obtained for the resin XAD-4, multiplied by 100. In other words, the recovery in the resin A-27 is related with the total of compound that eluted of the resin XAD-4 and that it was added to the top of the column with the resin A-27.

The relative retention of benzoic acid in the A-27 column is 100% while methyl valeric acid is only 1.3%. The presence of an aromatic ring in the benzoic acid structure appears to be the main cause of its higher retention on the Amberlyst A-27 stationary phase. Resonance effects can make the benzoate ion more stable than the valerate ion.

On the other hand, the low retention of the alcohol by the Amberlyst A-27 can be explained by the weak acidic character of these compounds with consequent poor ionic interaction with the stationary phase.

4. Conclusions

The proposed application of ion-exchange resins for the selective extraction of benzoic acid from a complex matrix like landfill leachate has many advantages over other common techniques that employ organic solvents. This process is rapid, simple and of low cost. The use of minimum amounts of hazardous organic solvents reduces the operator health risks and the residues, that can be discarded, and, also, contributes for the better quality of the laboratory environment.

The extraordinary capability of the Amberlyst A-27 for the selective retention of benzoic acid can be owing to the chemical structure of this compound. This fact makes the application of this stationary phase very useful when the screening of benzoic acid is needed in samples where this compound appear in low concentrations.

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