

## **Nitrogen organic compounds: emergent chemicals in landfill leachate**

Eduardo Lovatel, Nathália Vieceli, Irajá do Nascimento Filho  
Caxias do Sul University, Centre of Technology and Exact Sciences, Environmental Sanitation Institute. Av. Francisco Getúlio Vargas, 1130, CEP 95070-560, Caxias do Sul, RS – Brazil, Tel. +55-54-3218-2100; fax: +55-54-3218-2507.  
e-mail: inascimf@ucs.br

The main purpose of this work is the extraction of nitrogen organic compounds from landfill leachate samples. The samples were subjected to liquid chromatography in preparative scale, using XAD-4™, Amberlyst A-27™ and A-15™ resins as stationary phases. The relative area of the chromatographic peaks of the nitrogen compounds were of 8.3 (XAD-4™), 5.4 (A-27™) and 62.6% (A-15™). The selective retention was studied by the employment of a standard solution (10 mg L<sup>-1</sup>) of N-methyl-4-ethylbenzenesulfonamide (EMBS), N-methyl caprolactm (NMC) and N-butyl-4-methylbenzenesulfonamide (BMBS). Those standards compounds were retained mainly in the XAD-4™ column, suggesting that the majority of the nitrogen compounds in the sample are strongly basic. The compounds were identified by the GC-MS (Gas Chromatography with Mass Spectrometer detector) library (Wiley). Hazardous nitrogen compounds like N,N alkylformamides, alkylpyridines and N,N alkylbenzenesulfonamides were identified.

### **1. Introduction**

Nitrogen organic compounds are used as raw materials in manufacture of herbicides, surfactants, drugs, explosives, dyes, polymers and other synthetic materials. The main concern about those compounds in environmental matrices is that someones are hazardous and of hard decomposition by soil and aquatic microorganisms. As examples, the N-benzenesulfonamides are suspect of human carcinogenic action (Encyclopedia of Chemical Technology, 1978) and the guanidine can induce carcinoma in rats (<http://http-server.niehs.nih.gov>). Many nitrogen compounds found in leachates from municipal landfills are of environmental concern and someones are capable of causing permanent injury and death (Brown and Donnelly, 1988). In a landfill, the organic pollutants can percolate with the landfill leachate (a liquid concentrate from the organic matter degradation). The landfill leachate presents high BOD (biochemical oxygen demand) and COD (chemical oxygen demand) and, in this way, its a potential contaminant for soil, superficial and ground waters (Murray, Rouse and Carpenter, 1981, Munro et al. 1997). In fact, the landfill leachate percolation is of special concern of underdevelopment countries where the majority of the landfills are unlined. Although many authors have reported the identification and quantification of organic compounds

and testing the landfill leachate toxicity (Yong, Mohamed and Warkentin, 1992, James and Stack, 1997, Bernard et al. 1996, Murray and Beck, 1990) the isolation of chemical Chapter 2 classes of organic compounds in pure fractions, by preparative liquid chromatography, is still difficult and time consumer. Because this, the number of works with this focus is very scarce in the literature. Some recent example of works describing the employment of Solid Phase Extraction (SPE) and Ion Exchange Chromatography (IEC) for the characterization of organic compounds in environmental matrices are Nascimento, von Mühlen, and Caramão (2001) and Nascimento et al. (2003). In this work, its presented the application of SPE and IEC for the isolation of nitrogen compounds from municipal landfill leachate samples. The selective retention was tested by the extraction of a mixture (10 mg L<sup>-1</sup>) of the standards N-ethyl-4-methylbenzenesulfonamide (EMBS), N-methyl caprolactam (NMC) and N-butyl-4-methylbenzenesulfonamide (BMBS). The nitrogen compounds in the real samples were identified by the GC-MS system library (wiley).

## **2. Materials And Methods**

### **2.1 Samples**

The leachate samples were collected from a municipal solid waste sanitary landfill located in Porto Alegre, Rio Grande do Sul, Brazil. The samples were monthly collected from mai/1999 to january/2001 (total collection volume: 300 L). At each collection, 1L of leachate was collected from 10 different points of the leachate aeration pool, in amber glass bottles with caps internally covered with aluminum foils. The samples were filtered at low pressure, maintained at 4C and protected of light until the extraction procedures (at maximum 24h after the collection). Aliquots of 100 mL of the 10 sample bottles were mixed to form a combined sample that was extracted by SPE and IEC. Reagents and solvents utilized in this work were of p.a. grade.

### **2.2 Resins treatment**

The Amberlyst A-27<sup>TM</sup> resin (10 g) was mixed with 50 mL of NH<sub>4</sub>OH in methanol (10% v/v (5ml/45ml)). This mixture was stirred by 3 min and after a few minutes in rest, was washed with 25 mL of the following solvents: methanol, water (until pH 7), acetone and n-hexane. The Amberlyst A-15<sup>TM</sup> resin (5 g) was mixed with 25 mL of HCl in methanol (10% v/v (2,5mL/22,5mL)) and stirred by 5 min to convert the sodium sulphonate group to sulphonic acid. The mixture remains in rest by 5 min and was washed with of the following solvents: ethanol (15 mL), water (until pH 7), dichloromethane (15 mL) and acetone (20 mL).

### **2.3 Solid phase extraction**

A glass column (15 cm long x 11 mm i.d.) was dry packed with 1g of XAD-4<sup>TM</sup> resin. This column was washed with 10 mL of a methanol/acetone mixture 30% v/v (3 mL methanol:7 mL acetone) and 30 mL of distilled water. 100 mL of the combined sample were extracted. After the extraction, the column was vacuum dried by 10 min and washed with 10 mL of n-hexane. This n-hexane fraction (fraction 1) was reserved. The analytes retained in the XAD-4<sup>TM</sup> column were extracted with 3 mL of the ethanol/acetone mixture (fraction 2). The fraction 2 volume was reduced to 1 mL by a gentle flux of ultra pure nitrogen.

## 2.4 Ion exchange chromatography

The fraction 1 volume was reduced to 5 mL and placed at the top of a second column (identical to the first) dry packed with 1g of the ion exchange A-27™ resin. This column was washed with 10 mL of n-hexane (fraction 3). The fraction 3 was reserved. The analytes retained in this column were extracted with 5 mL of the methanoic acid/diethyl ether mixture (fraction 4). The fraction 4 volume was reduced to 1 mL. Finally, the fraction 3 volume was reduced to 5 mL and placed at the top of a third column (identical to the first and second ones) packed with 1g of the ion exchange resin A-15™. This column was washed with 10 mL of n-hexane and the retained analytes was extracted with 2 mL of the isopropylamine/n-hexane 10% (v/v) mixture (fraction 5). This fraction volume was reduced to 1 mL. Aliquots of 1L of the fractions 2, 4 and 5 were injected (triplicate) in the GC-MS system. The characteristics of the XAD-4™, A-27™ and A-15™ resins are described in the table 1.

Table 1. Resins Characteristics

Resin	Active group	Maximum temperature (°C)	Surface area (m <sup>2</sup> /g)	Porous volume	Exchange capacity
XAD-4™	-	-	725	0.98 mL/g	-
A-27™	N(Me) <sub>2</sub> H <sup>+</sup> .Cl <sup>-</sup>	60(OH) 80(Cl)	65	51%	2.6 meq/g
A-15™	-SO <sub>3</sub> <sup>-</sup> . H <sup>+</sup>	120	50	47%	3.3 meq/g

## 2.5 SPE/IEC of the standards compounds

A volume of 10 mL of a 100 mg L<sup>-1</sup> standards solution (EMBS, NMC and BMBS) in dichloromethane was diluted in 90 mL of distilled and deionized water. This solution was extracted in the same way that the real samples. The eluents volumes were of 20 mL for ensure the total elution. After volume reduction to 1mL, 1L of these extracts were analyzed in the GC-MS system.

## 2.6 Instrumental Analysis

The instrumental analysis was performed in a Shimadzu GCMS-QP5050A Gas chromatograph/Mass Spectrometer Detector equipped with a split/splitless injector operating in a split mode with ratio of 1:50 and electronic impact at 70 eV. A DB-5 capillary column (30m x 0.25mm i.d. x 0.25µm film thickness) was temperature programmed from 65 °C (hold 3 min) to 200 °C at 3 °C min<sup>-1</sup> and from 200 °C to 300 °C at 5C min<sup>-1</sup> (hold 10 min). Helium was the carrier gas with a flux of 1mL/min.

## 3. Results

Figure 1 show the chromatograms (SCAN mode) of the real samples organic extracts (A = XAD-4™, B = A-27™ and C = A-15™ columns). The numbered peaks in figure 1 are of nitrogen compounds (identified in the table 2). As can be observed in the table 2, 62.6% of the nitrogen compounds were retained mainly in the Amberlyst A-15™ column showing a high selectivity of this stationary phase for nitrogen compounds. Three classes of nitrogen compounds classified by Brown and Donnelly (1988) as of environmental concern, namely N,N alkylformamides, alkylpyridines and N,N alkylbenzenesulfonamides, were also identified. In a work published by Yasuhara et al. (1997) several organic nitrogen compounds were identified in leachates from hazardous waste disposal sites. Although the extraction method was different (liquid-liquid extraction - LLE) and that the individual nitrogen compounds are not the same, the

nitrogen class compounds found in this study are in good agreement with that found by Yasuhara. It was observed a higher retention of the nitrogen standard compounds in the XAD-4™ resin (6.9 mg L<sup>-1</sup>, for NMC, 6.5 mg L<sup>-1</sup> for EMBS and 7.9 mg L<sup>-1</sup> for BMBS). The retention in the Amberlyst A-27™ resin was of 0.2 mg L<sup>-1</sup> for NMC, 2.5 mg L<sup>-1</sup> for EMBS and 0.3 mg L<sup>-1</sup> for BMBS. The only one standard compound retained in the Amberlyst A-15™ resin was the EMBS (traces). This result can be explained by the fact that nitrogen compounds bearing a sulphur atom like EMBS and BMBS are weakly basic (Rosset et al. 1978). In NMC case, the adjacent C=O bond can difficult the proton transfer to the nitrogen atom. These results suggest that the acid resin Amberlyst A-15™ works well when the target compounds are strongly basic but fails in the retention of neutral or weak basic nitrogen compounds.

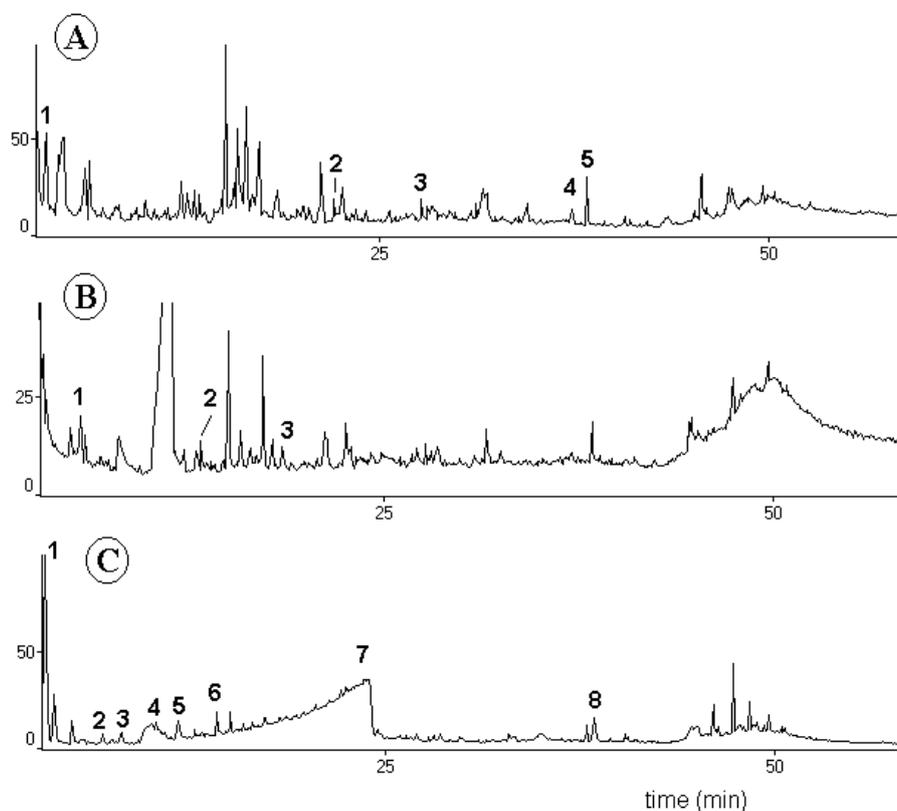


Figure 1. TICs of the extract obtained by SPE and IEC of the samples. A = fraction 2, B = fraction 4, C = fraction 5.

Table 2. Nitrogen organic compounds identified (GC-MS library) by samples SPE and IEC

Stationary phase	# peak	Compound	Match quality (%)	Area (%)
XAD-4 <sup>TM</sup> (A)	1	N,N-dimethylformamide	96	1.9
	2	3-propylpyridine		
	3	N,N,4-trimethylbenzenesulfonamide	77	1.4
	4	N,N-diethyl-1-butanamine	88	1.0
	5	1H-purine-2,6-dione-tetramethylxantine	73	2.9
	Total	-	-	8.3
A-27 <sup>TM</sup> (B)	1	Dimethyl amine diaxaspyro undecenone	85	1.1
	2	Isoamyl nitrate	72	1.5
	3	2-ethyl-(2,3-dimethyl-3-nitroso)	75	2.8
	Total	-	-	2.4
A-15 <sup>TM</sup> (C)	1	2-methylpropanamide	87	10.9
	2	Benzenaminium	69	1.6
	3	3-methylbutyl nitrite	83	2.1
	4	4-acetyl morfoline	85	3.7
	5	1,3-diisopropylurea	92	8.1
	6	N,N'-diisopropylloxiamide	83	5.6
	7	N-methyl metanamide	87	25.7
	8	1H-purine-2,6-dione-tetramethylxantine	76	4.9
	Total	-	-	62.6

#### 4. Conclusions

The results of this work show that the conjugation of the SPE and IEC methods is rapid, easy, cost safe and produce good nitrogen organic compounds isolation from complex samples as municipal landfill leachate. Although more standards compounds have to be tested, the results with the real samples suggest that, the resin Amberlyst A-15<sup>TM</sup> works very well for strongly basic nitrogen compounds retention while the XAD-4<sup>TM</sup> and A-27<sup>TM</sup> resins allows good retention of neutral and low basicity nitrogen compounds, respectively. The isolation of nitrogen compounds of environmental concern as N,N alkylformamides, alkylpyridines and N,N alkylbenzenesulfonamides from landfill samples was achieved by the employment of the SPE/IEC conjugated methods. The SPE/IEC conjugated methods give retention of about 70, 90 and 80% of NMC, EMBS and BMBS, respectively, in a 10 mg L<sup>-1</sup> standards mixture, in the XAD-4<sup>TM</sup> and A-27<sup>TM</sup> resins.

## **Acknowledgment**

The authors thank to CAPES, FAPERGS, University of Caxias do Sul and CNPq.

## **References**

- Bernard, C., P. Guido, J. Colin and D. AnneL, 1996, *Chemosphere*, 33, 2303.
- Brown K.W., and K.C. Donnelly, 1988, *Hazardous waste & hazardous materials*, 5, 1.
- Encyclopedia of Chemical Technology, third edition, John Wiley & Sons, New York, 1978.
- <http://htp-server.niehs.nih.gov>
- James, K.J. and M.A. Stack, 1997, *Chemosphere*, 34, 1713.
- Munro, I.R.P., K.T.B. MacQuarrie, A. J. Valsangkar and K.T. Kan, 1997, *Can. Geotech. J.* 34, 204.
- Murray, H.E. and J.N. Beck, 1990, *Enviromental Pollution*, 67, 195.
- Murray, J.P. J.V. Rouse and A.B. Carpenter, 1981, *Water Research*, 15, 745.
- Nascimento I.F., C. von Mühlen, P Schossler and E.B. Caramão, 2003, *Chemosphere*, 50, 657.
- Nascimento I.F. C. von Mühlen, and E.B. Caramão, 2001, (abstract in English) *Quím. Nova*, 24, 554.
- Rosset, R., M. Caude, J.C. Escalier and C. Bollet, 1978, *J. of Chromatogr.*, 167, 125.
- Yasuhara, A., H. Shiraishi, M. Nishikawa, T. Yamamoto, T. Uehiro, O. Nakasugi, T. Okomura, K. Kenmotsu, H. Fukui, M. Nagase, Y. Ono, Y. Kawagoshi, Baba K., Y. Noma, 1997, *J. of Chromatogr. A*, 774, 321.
- Yong, R.N.; A.M.O. Mohamed and B.P. Warkentin, 1992, *Principles of Contaminant Transport in Soils*, Elsevier, Netherlands.