Determination of anions in landfill leachates by ion chromatography

D.A.C. Manning*, A. Bewsher

Department of Earth Sciences, University of Manchester, Oxford Road, Manchester M13 9PL, UK

Abstract

Ion chromatography has been used to determine inorganic and organic anions within landfill leachates. Two procedures are operated on split samples which have multiple dilutions and vary in sample treatment: gradient ion-exchange chromatography for inorganic anions and isocratic ion-exclusion chromatography for organic anions. Interference between carbonate and organic acid anions using ion-exclusion chromatography is avoided by treatment with octanesulphonic acid eluent. Using ion-exchange chromatography, the presence of valerate, hexanoate and heptanoate is checked (but not quantified) for a subsample which has been treated to remove chloride; these species are then determined by ion-exclusion chromatography. Analysis of certified standards (10 mg/l certified VFA standard; Supelco, Bellefonte, PA, USA; 20–150 mg/l inorganic anions, ICMIX1-100, Glen Spectra Reference Materials, Middlesex, UK) gives good agreement (within 5% for organic anions except formate, and within 1% for inorganic anions), with R.S.D. values for all anionic species varying from 0.44–2.23.

Keywords: Environmental analysis; Inorganic anions; Organic anions; Volatile fatty acids; Fatty acids

1. Introduction

The disposal of waste by landfill is widely practised and has been carried out for many years, during which time standards of containment and management have changed [1,2]. Volumetrically, domestic waste is subsidiary to industrial waste, but its disposal usually takes place close to population centres where there are also pressures to redevelop landfill sites once completed [3]. An essential aspect of the disposal of domestic waste is its stabilisation, a general term for the processes of compaction and decay of putrescible material (such as food and plant waste). Stabilisation involves microbiologically-mediated decomposition of organic material, under anaerobic conditions, with methane and carbon dioxide as ultimate products [1]. Landfill leachates represent an important participant this process, being

the aqueous phase which provides anaerobic bacteria with the nutrients that they require as well as providing a means for transport of metabolic products. Typical compositions are given in Table 1. Landfill methane, produced via leachate degradation, is widely exploited as an energy source, or needs to be flared or vented to reduce the risk of explosions.

Leachate containment is an important aspect of landfill management. In modern sites, with good containment, the volatile fatty acid (VFA) contents of leachate are obtained partly to monitor the stabilisation process so that the onset of methane formation can be determined. Soon after the deposition of waste, the VFA contents of immature leachates are high. After a period of a few years they reduce to very low levels in mature leachates. In leachates from old landfills (or leaking from landfill), the VFA contents provide an indication of the maturity of the leachate and the potential of the site to produce methane, a factor which needs to be considered in

---

*Corresponding author.

Table 1
Summary of leachate compositions for 23 samples reported by Robinson [7], illustrating reported chemical species and typical values

	Minimum	Maximum	Mean
pH value	6.2	7.6	–
COD	66	11 600	2094
BOD	<2	8000	1314
TOC	21	4440	792
Volatile fatty acids (as C)	<2	3672	540
Acetic	nd	1321	219
Propionic	nd	1371	131
Isobutyric	nd	237	22.4
n-Butyric	nd	562	69.5
Isovaleric	nd	234	34.5
n-Valeric	nd	302	36.7
Isohexanoic	nd	9.4	1.2
n-Hexanoic	nd	197	25.8
Ammoniacal-N	5	730	151
Nitrate-N	<0.4	85	4.3
Nitrite-N	<0.02	1.84	0.2
Orthophosphate (as P)	<0.02	4.43	0.46
Chloride	70	2777	782
Sulphate	55	465	242
Sodium	43	2500	610
Magnesium	12	480	126
Potassium	20	650	208
Calcium	130	1150	369
Chromium	<0.005	0.14	0.037
Manganese	0.19	26.5	3.79
Iron	0.09	380	75.2
Nickel	<0.02	0.16	0.03
Copper	0.004	0.15	0.02
Zinc	0.02	0.95	0.23
Cadmium	0.003	0.013	<0.005
Lead	0.003	0.22	0.06

COD=chemical oxygen demand.
BOD=biochemical oxygen demand (5 day test).
TOC=total organic carbon.
All values in mg/l (except pH).

redevelopment plans. Leachate compositions also provide an indication of the reactions which take place within mineral seals and waste, with long term implications for stabilisation and containment [4].

The VFA population which occurs within leachates is dominated by acetate and/or propionate, with successively lower amounts of higher homologues of monovalent carboxylic acids. Acetate contents can reach 10 000 mg/l and propionate 3000 mg/l. Other anions include chloride (<10 000 mg/l), sulphate (<2000 mg/l) and bicarbonate (often expressed as alkalinity, <9000 mg/l $CaCO_3$). The dominant cations are Na, K, Mg and Ca, and the proportions of these are largely controlled by mineral dissolution-precipitation reactions [4]. Other important components of leachates include humic acids, colloidal and suspended matter. There are a number of surveys of leachate composition which do not give full details of analytical procedures [4–7], and other analytical work on leachates has focused on specific analytes (e.g., Cl^-, NO_2^-, NO_3^- and SO_4^{2-}, [8]; VFA [9,10]). This paper provides an opportunity to report

an integrated approach to the determination of anions in leachates by ion chromatography.

2. Experimental

2.1. Sample collection and storage

The leachates used in this study were obtained from commercial landfill sites in Cheshire, UK [4]. All were within 60 min by road from the analytical laboratory, and sampling was timed to coordinate with adequate periods of instrument availability. Using a stainless-steel bailer, the leachates were taken from inspection wells, up to 30 m deep, within which the leachate depths reached about 1 m, below an atmosphere rich in CO_2 and CH_4. Initial filtering of coarse suspended material was carried out on site using a nylon sieve (nominal 1 mm aperture) prior to bottling in flexible polythene bottles from which air was excluded by squeezing. On the day of sampling, further filtration and dilution was undertaken in the laboratory, as summarised in Fig. 1. The samples were stored in a refrigerator at 4°C with determination of organic species as soon as possible after sampling (usually within 48 h). Preservatives were not used, partly because of the lack of efficacy under anaerobic conditions of widely-used preservatives (Hg precipitates as sulphide, sodium azide is not effective against anaerobic bacteria [11], and dichloromethane or chloroform appear to have no effect), and partly because decomposition of VFA species was not found to be a problem. Additionally, variation in leachate composition is more likely to arise from heterogeneity within landfill sites rather than changes after sampling [7].

2.2. Apparatus

Two ion chromatographs were used for the determination of anions. A Dionex 4000i equipped for gradient operation, with the Dionex AS11 column (following earlier use of the AS5A) and automatic eluent regeneration, was used for inorganic anions and to screen for organic acid anions. Samples were loaded automatically using a Dionex autosampler. A Dionex QIC (isocratic) with the Dionex ion-exclusion column AS-ICE 1 was used for organic acid
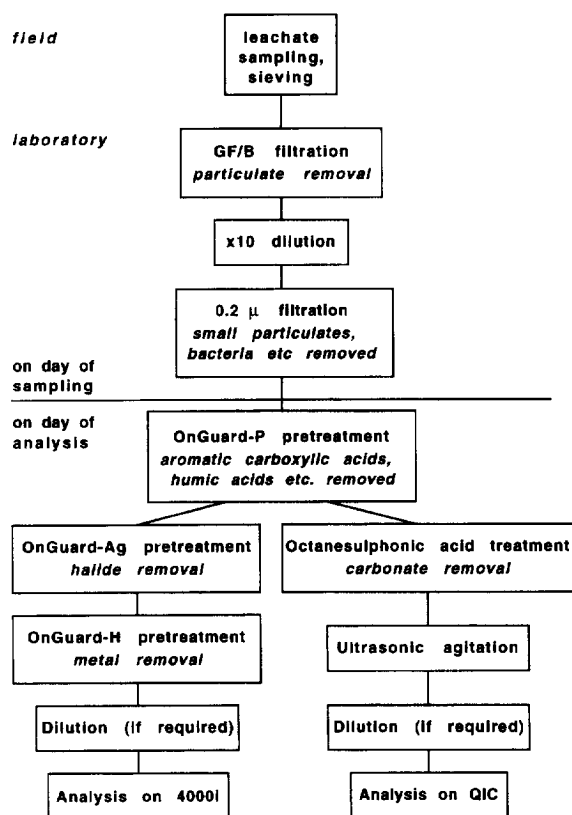

Fig. 1. Flow sheet summarising pretreatment procedures and route taken by leachate samples. "GF/B filtration" refers to the type of Whatman glass fibre filters used for filtration.

anions, with manual sample injection. In both cases, conductivity detection was used, with integration and data management using a Dionex AI450 data station.

2.3. Chemicals

Sodium hydroxide (50%) solution was purchased from Merck/BDH (Poole, UK) and used to produce eluents for the 4000i system (0.75 mM NaOH and 200 mM NaOH). For the QIC, octanesulphonic acid (OSA; 0.1 M) was purchased from Dionex (Camberley, UK), and diluted to give 1 mM eluent. Tetrabutylammonium hydroxide (TBAOH; 40% solution) was purchased from Sigma–Aldrich (Poole, UK) and diluted to 10 mM for use as regenerant. Standards for instrument calibration were made from analytical grade chemicals where available, or general purpose reagents ("AnalaR" sodium fluoride, potassium

D.A.C. Manning, A. Bewsher / J. Chromatogr. A 770 (1997) 203–210

chloride, potassium sulphate, sodium nitrite, ammonium nitrate, potassium dihydrogen phosphate; "GPR" propionic acid, sodium formate, sodium n-butyrate, sodium thiosulphate; Merck/BDH; isobutyric acid, isovaleric acid; Fisons, Loughborough, UK; isohexanoic acid, hexanoic acid, isoheptanoic acid, heptanoic acid; Sigma–Aldrich; n-valeric acid; Fluka, Gillingham, UK). As an independent test of accuracy, certified standards were purchased and run as unknowns (20–150 mg/l inorganic anions, ICMIX1-100, Glen Spectra Reference Materials, Middlesex, UK, and 10 mg/l organic anion standard prepared to order by Supelco, Bellefonte, PA, USA). High purity water was used for all dilutions of standards and samples, and to make up eluents (18.2 MΩ; Elga).

2.4. Analytical procedures

Prior to instrumental analysis, the sample was passed through a Dionex OnGuard-P cartridge to remove aromatic carboxylic acids, humic acids and other potential column contaminants. The sample was then split to follow two routes. In the first route, inorganic anion determinations were made using the 4000i system, using a gradient programme (an example is given in Table 2). An initial run at high dilution was made to estimate appropriate dilutions for the subsequent quantitative determination of chloride (Fig. 2). Then, after pretreatment with Dionex OnGuard-Ag and OnGuard-H cartridges to remove chloride and metals, respectively, a further run is used to quantify sulphate and other inorganic
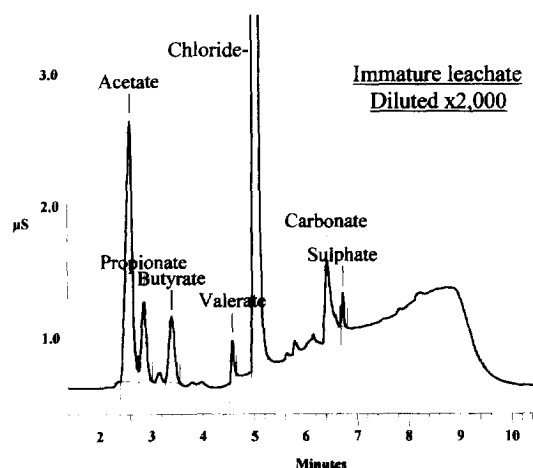

Fig. 2. Ion chromatogram (4000i/AS11 gradient) for immature leachate (×2000 dilution).

anions (Fig. 3). The removal of chloride allows peaks for valerate, hexanoate and heptanoate, to be observed (Fig. 3), but they are not quantified. If these organic anions are observed, sufficient time can then be allowed for their determination using the QIC (retention times for these species are very long; Table 3). Organic acid anion contents are low in mature leachates, as shown in Fig. 4. Determinations using the 4000i typically used gradient programmes with approximately 15 min between sample injection.
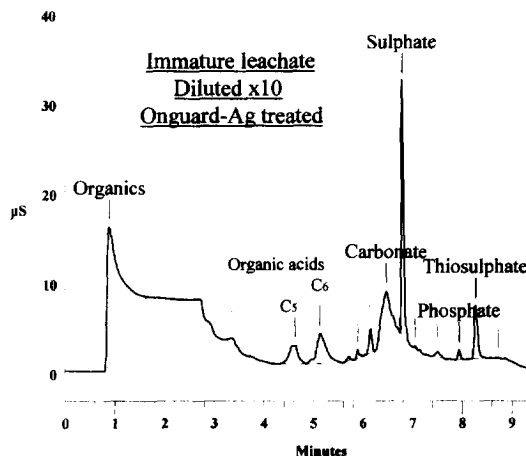
For determination of some VFA species, interfer-

Table 2
Typical gradient programme used for inorganic anions (Dionex 4000i with AS11 ion-exchange column)

Time (min)	Injection valve	E1 (%)	E2 (%)	E3 (%)
0.0	off	50	0	50
0.1	on	50	0	50
0.2	off	50	0	50
2.0	off	50	0	50
7.0	off	85	15	0
7.1	off	50	0	50

Eluent E1: 18 MΩ water.
Eluent E2: 200 mM NaOH.
Eluent E3: 0.75 mM NaOH.
Eluent flow-rate: 2 ml/min; sample loop: 50 μl.

Fig. 3. Ion chromatogram (4000i/AS11 gradient) for immature leachate (×10 dilution).

Table 3
Accuracy based on 3 determinations of organic acid anions for a certified standard (na indicates not available)

Analyte	Typical retention time (min)	Reference (mg/l)	Observed (mg/l)
Formate	11.5	10.0	8.4
Acetate	13.1	10.0	9.8
Propionate	15.4	10.0	9.6
Isobutyrate	17.1	10.0	9.9
n-Butyrate	19.1	10.0	9.6
Isovalerate	21.9	10.0	10.0
n-Valerate	28.4	10.0	9.7
Isohexanoate	38.2	10.0	10.3
n-Hexanoate	46.7	10.0	9.8
Isoheptanoate	54.7	na	–
n-Heptanoate	86.0	10.0	9.2

Isocratic chromatography; Dionex QIC/HPICE-AS1 column/conductivity detector; 1 mM octanesulphonic acid eluent/10 mM TBAOH regenerant.

Fig. 5. Ion chromatogram (QIC/HPICE-AS1, isocratic) for immature leachate (×40 dilution), showing large carbonate peak which may obscure VFA species (see Fig. 6).

ence with carbonate (as shown in Fig. 5) needs to be avoided. This is achieved by addition to the sample of an equal amount of the octanesulphonic acid eluent, followed by allowing to stand overnight and ultrasonic agitation for up to 15 min, then dilution prior to analysis. Fig. 6 shows that the removal of carbonate permits quantification of isobutyrate (which previously had been masked altogether) and improves the baseline for butyrate and isovalerate. Because of the long retention times of some species (Table 3), sample injections are commonly at inter-
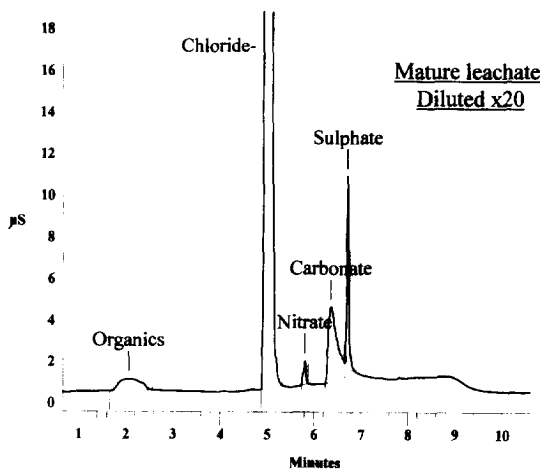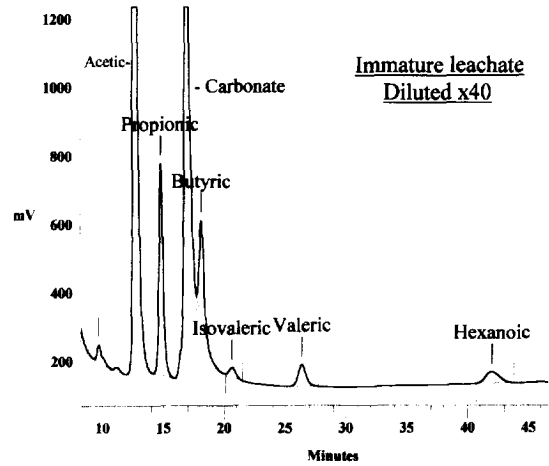
vals in excess of 100 min (if high relative molecular mass species are present they may interfere with subsequent samples, emphasising the need to seek such species using the gradient run on a chloride-free sample).

3. Results and discussion

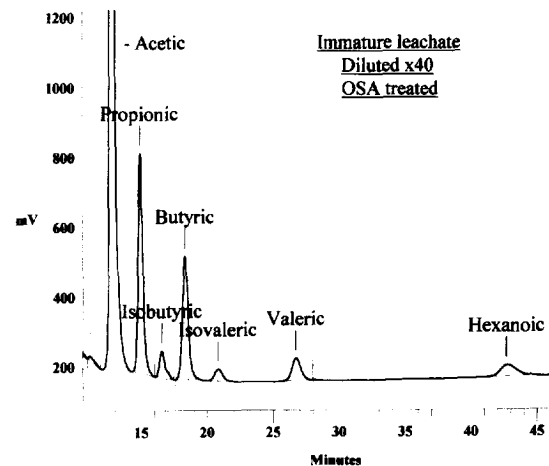Further details of the results obtained using the

Fig. 4. Ion chromatogram (4000i/AS11 gradient) for mature leachate (×20 dilution).

Fig. 6. Ion chromatogram (QIC/HPICE-AS1, isocratic) for immature leachate after removal of carbonate (×40 dilution; compare with Fig. 5).

methods outlined here are presented in a detailed study of leachate variability over a period of 2 years [4,12]. Other studies of anions within leachate focus on specific species (Cl^-, NO_2^-, NO_3^- and SO_4^{2-}, [8]), or do not consider ion chromatographic techniques [13,14]. A major advantage of the ion chromatographic methods used here is that species which are not requested may be reported in the chromatograms, giving a more complete analysis. This contributes to quality evaluation by charge balance assessment (an essential first step in the screening of water analyses).

Analysis of a 10 mg/l certified VFA standard (Supelco) using the methods described here indicates that the results for most species agree with reference values within 5% (Table 3). One exception is formate, which is very unstable in solution and which may have decomposed after opening the certified standard's vacuum-sealed vial. The poor result for heptanoate may be a consequence of peak broadening, which increases with increasing relative molecular mass. Precision for VFA species has been estimated by repeat analysis of 10 mg/l standards (Table 3). For these anions, 10 mg/l stock solutions are unstable, and so the R.S.D. values given in Table 4 are based on serial analysis where a new dilution from a stock 1000 mg/l standard was made for each determination. In practise, leachate VFA contents often greatly exceed 10 mg/l, and dilution for analysis should be carried out immediately before injection, with no storage after dilution. Detection limits for VFA species in leachates are approximately 5 mg/l.

Table 4
Precision based on repeat determination of organic anion standards (5 determinations)

Analyte	R.S.D. (%)
Formate	0.58
Acetate	0.62
Propionate	0.44
Isobutyrate	0.98
n-Butyrate	1.38
Isovalerate	1.41
n-Valerate	2.07

Isocratic chromatography; Dionex QIC/HPICE-AS1 column/conductivity detector, 50 μl sample loop; 1 mM octanesulphonic acid eluant/10 mM TBAOH regenerant.

Table 5
Accuracy for determination of inorganic anions

	Observed values (mg/l)	Certified values (mg/l)
Fluoride	20.17	20.15
Chloride	30.11	30.05
Nitrate	99.22	99.58
Sulphate	148.13	149.44
Phosphate	149.15	148.86

Gradient chromatography; Dionex 4000i/AS11 column/conductivity detector; NaOH eluent (Table 1) with autoregenerant.

Analysis of a certified standard for inorganic anions (Table 5) shows observed values lying within 0.4% of reference values. R.S.D. values range up to 2.2% for concentrations which vary from species to species to give similar instrumental response (Table 6).

In other methods used for the determination of VFA species, liquid or gas chromatographic methods have been used to determine acids separated either by distillation [9,10] or derivatisation [15,16]. In both cases recoveries may be difficult to assess or are reported to be low [11], requiring the use of techniques such as standard addition. However, one advantage of distillation coupled with HPLC–UV rather than GC in the determination of VFA species in leachate is that formic acid can be determined [9]. Ion chromatographic methods as reported here would also detect formate, but formate has not been observed in other studies and may be absent from the leachates considered in this study [7].

For inorganic anions, ion chromatography has particular advantages over other methods for the determination of sulphate. Standard methods using

Table 6
Precision based on repeat determination of inorganic anion standards (5 determinations)

Analyte	Average concentration (mg/l)	R.S.D. (%)
F^-	2.13	1.23
Cl^-	3.12	0.68
NO_3^-	10.32	2.23
SO_4^{2-}	15.61	0.95
PO_4^{3-}	15.35	1.46

Gradient chromatography; Dionex 4000i/AS11 column/conductivity detector; NaOH eluent (Table 1) with autoregenerant.

autoanalysers depend on turbidometry (or colorimetry [14]), and the inherent turbidity of leachates causes substantial interference [7]. However, the differences between leachate contents of chloride and other inorganic anions are so great that it is unusual to be able to determine all inorganic anions for one sample dilution. Fluoride can be determined using either the gradient or the isocratic methods described here, and for some samples the isocratic method has advantages (fluoride clearly elutes before formate, whereas in the gradient method there may be interferences with other early-eluting species). No fluoride has been observed in the landfill leachates used in this study.

The major disadvantages with the ion chromatographic methods outlined in this paper are two-fold. First, despite the precaution of pretreatment with OnGuard-P cartridges, column fouling on the 4000i is a frequent problem, which is overcome using a rigorous acid cleanup procedure on completion of a batch of leachate analyses. Fouling does not affect the HPICE-AS1 column, from which VFA data are obtained. Secondly, the use of pretreatment cartridges, coupled with multiple dilutions and repeat runs for each sample, means that the cost per sample of performing the analysis is relatively high. These disadvantages may be outweighed by the need to obtain data of a particular quality.

Typical results for anions in leachates determined using the techniques described in this paper are given in Table 7.

Finally, it is important to note that the sampling procedures used for leachate collection may influence analytical results. There appears to be no advantage to be gained by using apparatus more sophisticated than a bailer, as differences in leachate composition which have been observed in comparative studies are attributed to variation in the microenvironments that are accessible to different sampling techniques, rather than changes as a consequence of the sampling operation [7,17].

4. Conclusions

Ion chromatography provides a satisfactory method for the determination of anions within landfill leachates, provided that sample pretreatment is carried out to reduce column fouling, and to remove carbonate and chloride for determination of coeluting species. In particular, use of ion-exclusion chromatography for the determination of VFA species appears to be robust and avoids problems of column fouling.

References

[1] J.F. Rees, Chem. Technol. Biotechnol., 30 (1980) 161–175.
[2] Department of the Environment, Waste Management Paper No. 1: A Review of Options, Her Majesty's Stationery Office, London, 1992.
[3] Department of the Environment, Waste Management Paper No. 26: Landfilling Wastes, Her Majesty's Stationery Office, London, 1986.
[4] J.A. Owen and D.A.C. Manning, App. Geochem., in press.
[5] G.J. Farquhar, Can. J. Civ. Eng., 16 (1989) 317–325.
[6] G. Andreotolla and P. Calas, in T.H. Christensen, R. Cossu and R. Stegmann (Editors), Landfilling of Waste: Leachate, Elsevier Applied Science, London, 1992, Ch. 2.4, pp. 65–88.
[7] H.D. Robinson, A Review of the Composition of Leachates from Domestic Wastes in Landfill Sites. Project Report DE0918A/FR1, Department of the Environment, London.
[8] B. Gade, J. Chromatogr., 640 (1993) 227–230.
[9] J.F. Jen, C.W. Lin, C.J. Lin and C.T. Yan, J. Chromatogr., 629 (1993) 394–397.
[10] C.T. Yan and J.F. Yen, Anal. Chim. Acta, 264 (1992) 259–264.
[11] M. Rozycki and R. Bartha, Appl. Environ. Microbiol., 41 (1981) 833–836.
[12] J.A. Owen and D.A.C. Manning, Anal. Proc. Inc. Anal. Comm., 31 (1994) 277–278.
[13] U. Lund, L. Rasmussen, H. Segato and P. Østfeldt, in T.H. Christensen, R. Cossu and R. Stegmann (Editors), Landfilling of Waste: Leachate, Elsevier Applied Science, London, 1992, Ch. 2.9, pp. 167–181.

Table 7
Examples of anion compositions (mg/l) of leachates determined by ion chromatography [4]

	Immature	Intermediate	Mature
Chloride	8830	2060	650
Sulphate	1720	5	10
Acetate	6940	670	0
Propionate	2810	200	0
Isobutyrate	320	0	0
n-Butyrate	3380	5	0
Isovalerate	280	5	0
n-Valerate	1460	5	0

[14] American Public Health Association, American Water Works Association and Water Pollution Control Federation, Standard Methods for the Examination of Water and Waste Water, American Public Health Association, Washington, DC, 1995.

[15] K. Kawamura, S. Steinberg and I.R. Kaplan, Int. J. Environ. Anal. Chem., 19 (1985) 175–188.

[16] M.A. Lambert and C.W. Moss, J. Chromatogr., 74 (1972) 335–338.

[17] H.D. Robinson and J.L. Lucas, Water Poll. Res. J. Canada, 20 (1985) 76–91.