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# Ion chromatographic investigations of leachates from a hazardous-waste landfill

Beate Gade

*Forschungs- und Entwicklungszentrum Sondermüll, Siemensstrasse 3–5, D-8540 Schwabach (Germany)*

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## ABSTRACT

Leachates from different areas of a modern hazardous-waste landfill were investigated. In addition, samples of the waste to be buried were taken, and leachability tests in accordance with German standards were performed. The composition of the leachates from the landfill and the leachates produced by the leachability tests varied over a wide range, depending on the kind and volume of hazardous waste buried and the weather conditions. High concentrations of some anions were often found in combination with low concentrations of other anions. In the leachates the following concentration ranges were found:  $\text{Cl}^-$ , 30–6000 mg/l;  $\text{NO}_2^-$ , 0–150 mg/l;  $\text{NO}_3^-$ , 0–150 mg/l;  $\text{SO}_4^{2-}$ , 100–6000 mg/l. Therefore, several dilutions of one sample often had to be measured. The complex matrix often also requires several sample preparation steps for the elimination of interfering effects. Experience to date has shown that ion chromatography in this application field is efficient.

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## INTRODUCTION

The control of landfills, especially of hazardous waste landfills, is becoming increasingly important. Depending on the industrial structure of the region where the landfill is located, most of the hazardous wastes to be buried are electroplating sludges and wastewater treatment sludges. For environmental control purposes, the leachates from hazardous waste landfills and leachability test samples have to be analysed regularly. For this reason, a research project to investigate the input and the output of a modern hazardous waste landfill was carried out. Many parameters of leachates from different parts of the landfill were analysed. Ion chromatography (IC) was used for the analysis of the most important anions ( $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) in these samples.

## EXPERIMENTAL

### *Apparatus*

An isocratic ion chromatograph with a Waters 510 pump, a Waters 431 conductivity detector and a Waters 712 WISP autosampler were used. The analyses were carried out with a Waters IC PAK-Anion

column (50 × 4.6 mm I.D.) and a Waters RP  $\text{C}_{18}$  precolumn.

### *Chemicals*

Gluconic acid [50% (w/w) solution] and lithium hydroxide monohydrate (analytical-reagent grade) were purchased from Fluka (Buchs, Switzerland). Boric acid (analytical-reagent grade) and glycerine [87% (w/w) solution, analytical-reagent grade) were obtained from Merck (Darmstadt, Germany); acetonitrile (Chromasolv) was from Riedel-de Haen (Seelze, Germany).

### *Procedure*

A single-column separation with subsequent direct conductivity detection was carried out [1]. A borate-gluconate eluent was used [2–5]. The borate-gluconate eluent concentrate was prepared with 17.0 g of boric acid, 11.75 ml of gluconic acid [50% (w/w) solution], 4.3 g of lithium hydroxide monohydrate and 62.5 ml glycerine and made up with purified water (Milli-Q, Millipore) to 500 ml. The eluent was prepared by adding 14 ml of eluent concentrate to 120 ml of acetonitrile and made up to 1000 ml with purified water. The mobile phase was

TABLE I  
CONCENTRATION RANGE AND ANALYTICAL CONDITIONS

Samples to be measured	Concentration range (ml/l)	Dilution	Measures to be taken against interferences	
Leachability test samples of different hazardous wastes, mainly electroplating sludges	Cl <sup>-</sup>	30-4500	1:10	Sample preparation filtration 45 μm cation exchanger standard addition
	NO <sub>3</sub> <sup>-</sup>	10-150	1:100	
	SO <sub>4</sub> <sup>2-</sup>	300-5500	1:500	
	NO <sub>2</sub> <sup>-</sup>	10-150	1:1000	
Leachates from the hazardous waste landfill	Cl <sup>-</sup>	1200-6000	1:10	Sample preparation filtration 45 μm, cation exchanger standard addition
	NO <sub>3</sub> <sup>-</sup>	30-300	1:100	
	SO <sub>4</sub> <sup>2-</sup>	300-1600	1:500	
	NO <sub>2</sub> <sup>-</sup>	10-150	1:1000	
Leachates from the hazardous waste landfill; monodisposal	Cl <sup>-</sup>	0-60	1:10	Sample preparation filtration 45 μm, cation exchanger; after IC run, cleaning column with eluent concentrate
	NO <sub>3</sub> <sup>-</sup>	0-30	1:100	
	SO <sub>4</sub> <sup>2-</sup>	100-2500	1:500	

degassed by vacuum filtration through a Nuclepore filter of 0.45 μm pore size.

The chromatographic separation was carried out at a flow-rate of 1 ml/min isocratically. The run time of the first runs was 20 min; later the run time was shortened to 15 min. Overlapping of the peaks of chloride and/or sulphate with the peaks of anions with lower concentrations often occurred at shorter run times. Therefore, further optimization of the run time was not possible. The injection volume was 50 μl. In general, the analyses were done twice. If necessary, the measurements were repeated. The analytical conditions are shown in Table I.

#### Sample preparation

The leachability test samples were produced by adding 1 l of purified water to an amount of a (wet) hazardous waste sample equivalent to 100 g of dry substance. The sample and the water were placed in a 2-l polyethylene bottle. The bottles were rotated at a speed of 1 rpm in a rotation apparatus for a period of 24 h [6]. After filtration, the leachability test samples were analysed.

For sampling the leachate, computer-controlled automatic samplers are installed at the landfill site. Random samples and weekly average samples were taken. The samples were filtered through a filter of 45 μm pore size and diluted. For the sample preparation of some leachates, especially leachates pro-

duced in a monodisposal area of the landfill, a Millitrap H<sup>+</sup> cation exchanger was used.

#### Standards

The standards were made using sodium chloride, sodium bromide, sodium nitrite, sodium nitrate, potassium dihydrogenphosphate and sodium sulphate, all analytical-reagent grade. Prior to the preparation of the standard solutions, sodium nitrate, potassium dihydrogenphosphate and sodium sulphate were dried at 105°C; sodium chloride, sodium bromide and sodium nitrite were dried at 150°C in accordance with German Industrial Standards [7].

The standard solutions for the calibrations were prepared in the concentration range 2-20 mg/l. The linearity range of the calibration curves was tested with a variance homogeneity test. The calibration curves were found to be linear in the above-mentioned range.

#### RESULTS AND DISCUSSION

Different leachates are produced in different areas of the hazardous waste landfill. Most of the leachate is produced in an area where various kinds of hazardous waste are buried. These leachates can generally be treated like the leachability test samples, although the concentrations of the anions in

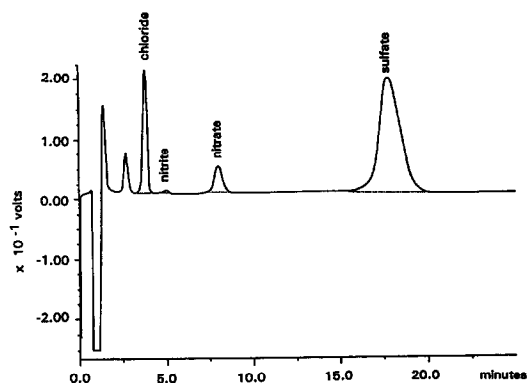


Fig. 1. Ion chromatogram of a leachability test sample of an electroplating sludge. Concentrations in the undiluted sample:  $\text{Cl}^-$ , 63.1 mg/l;  $\text{NO}_2^-$ , 3.2 mg/l;  $\text{NO}_3^-$ , 54.0 mg/l;  $\text{SO}_4^{2-}$ , 421 mg/l.

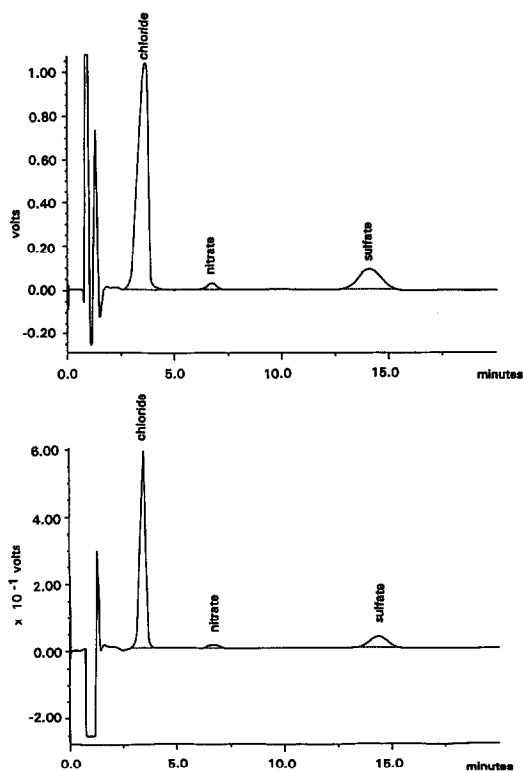


Fig. 2. Two examples of the concentration range in leachates from a hazardous waste landfill. Top: weekly average sample: dilution 1:10. Concentrations in the undiluted sample:  $\text{Cl}^-$ , 1365 mg/l (not quantified in this chromatogram but in a 1:100 dilution);  $\text{NO}_3^-$ , 66.6 mg/l;  $\text{SO}_4^{2-}$ , 355 mg/l. Bottom: random sample: dilution 1:100. Concentrations in the undiluted sample:  $\text{Cl}^-$ , 4280 mg/l;  $\text{NO}_3^-$ , 201 mg/l;  $\text{SO}_4^{2-}$ , 1057 mg/l.

the leachate are often higher than in the leachability test samples.

Owing to the diversity of hazardous wastes to be buried, there is a wide range of concentrations of the main anions  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Fig. 1 shows a typical ion chromatogram of a leachability test sample. In most cases, large amounts of chloride and sulphate and minor amounts of nitrate and sometimes nitrite are present.

Fig. 2 shows two typical chromatograms of a random and a weekly average sample. The most difficult to measure leachates were collected from a monodisposal area where special iron oxide sinters are buried. These leachates contain large amounts of metals and ammonium. It is necessary to use a cation exchanger for sample preparation for every sample. Fig. 3 shows an example of this leachate

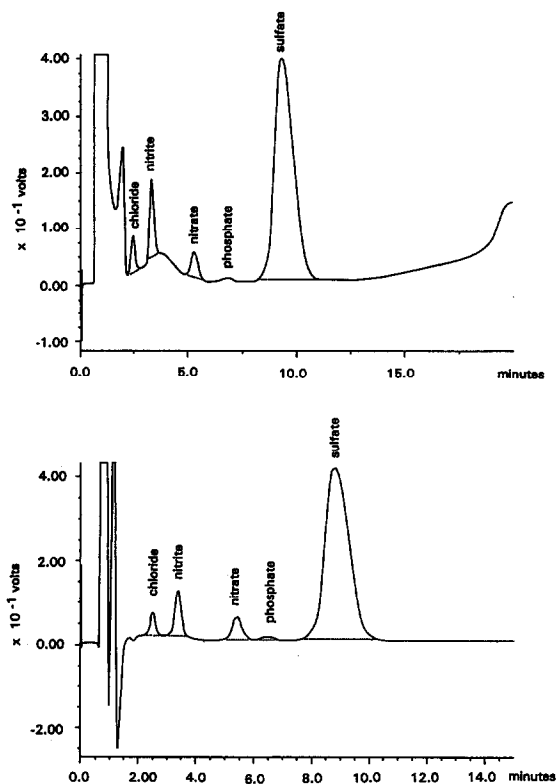


Fig. 3. Chromatograms of a leachate from a monodisposal area of the landfill. Top: without using a cation exchanger. Bottom: with using a cation exchanger. Concentration of the undiluted sample:  $\text{Cl}^-$ , 16.7 mg/l;  $\text{NO}_2^-$ , 59 mg/l;  $\text{NO}_3^-$ , 60.6 mg/l;  $\text{PO}_4^{3-}$ , 17.1 mg/l;  $\text{SO}_4^{2-}$ , 735 mg/l.

measured with and without the use of a cation exchanger for sample preparation.

Chromate contents can also cause interferences. To avoid drastic changes in pH, no other pretreatment measures were taken. If these samples are measured, runs are integrated in the automatically worked sample queue for cleaning the chromatographic system, e.g. by injecting eluent concentrate and purging for a sufficient time to avoid the delayed elution of interfering substances in the chromatogram of the following sample.

Because of the diversity of the hazardous wastes, it is necessary in many cases to check whether the chromatograms show the signals of the anions to be measured or interferences. In addition to the measures already mentioned, such as the use of ion exchangers and standard addition, other measurements such as photometry sometimes have to be carried out also to confirm the results of ion chromatography. Depending on the different kinds of samples, purging runs of differing lengths are integrated in the automatic measurements.

In addition, plausibility checks should be performed whenever possible. A direct correlation between the concentration of the anions and the amount of precipitation and leachate production can be found. High concentrations of the anions are associated with low amounts of leachate and *vice versa*. These results, provided by ion chromatography, are plausible because of the diluting effect of the rainwater on the leachate.

The results obtained so far can be summarized as follows:

Fluoride can in principle be measured by the method described above. As a result of a period of testing, the fluoride measurements are executed with a fluoride-sensitive electrode because of frequent interferences in this retention range that could not be removed completely.

Like fluoride, bromide and phosphate can be determined by this method. However, because of the composition of the hazardous wastes and the leachates of the landfill, they have rarely been found until now. Because of this, a final evaluation of the suitability of the analytical method for these ions cannot be given.

## CONCLUSIONS

Ion chromatography has proved to be a useful analytical method for the analysis of hazardous waste samples, especially eluates and leachates from a hazardous waste landfill. Nevertheless, it was necessary during the establishment of the analytical facilities to check the quality of the analyses of these samples with partially complex matrices using other analytical methods.

Special steps for the analysis of the different kinds of samples have been developed. Now a routine analysis of the ions  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  is done in a wide concentration range.

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