

Determination of organochlorine compounds in anion-exchange resins by UV irradiation and ion chromatography

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ABSTRACT

Anion-exchange resins may release organochlorine compounds during the demineralization of water in make-up plants. These substances can be decomposed by exposure to UV irradiation into chloride salts which can subsequently be determined by ion chromatography. The experimental conditions in the above method were studied and optimized. In addition, the method was validated using some organochlorine compounds of known structure. Finally, the method was applied to the determination of leachable organochlorine compounds in samples of anion-exchange resins.

INTRODUCTION

In one of the stages of ultrapure water production, water flows through a resin bed in a demineralizer. The structure of an anion-exchange resin consists of an aminated macropolymer, most commonly of the styrene-divinylbenzene type or an acrylic polyester. Leachable compounds in these resins may contaminate the water with organic substances. The fact that these contaminants are non-ionic makes them undetectable by conductivity or ion chromatographic methods.

If this water is intended for steam generation, these organic contaminants may undergo thermal decomposition under the conditions of pressure and temperature existing in the steam cycle. As a

result, chlorinated compounds release chloride ions into the water, which may lead to corrosion [1].

Three possible sources can be ascribed to these contaminants. During anion-exchange resin manufacture, chlorine-containing solvents are used, *e.g.*, ethylene dichloride. At a certain stage of its manufacture, the resin is a chlorinated macropolymer [2], this chlorine later being replaced with amine groups. However, residual solvents or chlorinated compounds from the manufacturing process may be retained within the resin structure. As they are non-ionic they will be released slowly into the water during demineralization and leak through the resin bed. In water chlorination during pretreatment, chlorinating reagents used as disinfectants may react with natural organic substances already present in water and result in volatile chlorinated compounds such as trihalomethanes (CHCl_3 , CHBrCl_2 , CHBr_2Cl , CHBr_3) [3]. Therefore, it is

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possible these substances are already present in the water supplied to the resin train demineralizer. Some power plant records give evidence of increases in steam water conductivity after new resins had been introduced into the demineralizer. The analysis revealed an increase in chloride ion concentration. As this water met the necessary specifications when introduced to the condensate, decomposition of organochlorine compounds seems to be the direct source of this increase [1]. To avoid these problems, it is necessary to check for very low levels of leachable organochlorine compounds in water.

The aim of this work was to develop a method that would achieve complete decomposition of organochlorine compounds into inorganic chloride, a method suitable for use in the laboratory that would enable one to predict the maximum amount of chlorine that might be measured in water by any other procedure. Ion chromatography with automatic sample preconcentration and conductimetric detection is a suitable technique that provides rapid and reproducible measurements of anion concentrations at the $\mu\text{g}/\text{l}$ level [4,5]. The chloride is leached into water matrices that may contain trace amounts of other inorganic ions such as sulphates, fluorides or carbonates and small amounts of organic matter. Such substances do not interfere in the determination of chloride by the proposed technique.

The test suggested in this paper [6] is basically carried out in two steps. First, the water sample (previously in contact with the resin) is exposed to UV irradiation, this causes decomposition of organochlorine compounds, releasing chloride ions. The second step is the determination of the increase in chloride ion concentration by ion chromatography. The difference in chloride concentration before and after irradiation is a measure of the amount of organochlorine contaminants present initially in the water sample. The best results were obtained when a helium atmosphere was maintained inside the lamp vessel during irradiation, which avoids atmospheric sample contamination. In addition, the method was validated for chlorinated compounds of known structure and several resin samples were analysed.

EXPERIMENTAL

Irradiation source

The UV lamp used was a Model TNN 15/32 Quartz Lampen 5631 (0.13A) low-pressure mercury lamp from Hanau Heraeus (Berlin, Germany) [7], with wavelength maxima at 254 and 170 nm with an intensity ratio of 6:1 (Fig. 1).

Chromatographic conditions

The analyses were performed with a Waters Model 590 ion chromatograph equipped with a Waters Model 430 conductivity detector. The background conductivity was $320 \mu\text{S}/\text{cm}$. The column was a Waters IC-Pak A Anion ($50 \text{ mm} \times 4.6 \text{ mm I.D.}$, $10 \mu\text{m}$ particle size) (Millipore, Bedford, MA, USA). The mobile phase was borate–gluconate (1.3 mM) buffer prepared according to the manufacturer's manual [8] at a flow-rate of $1.2 \text{ ml}/\text{min}$. Sodium gluconate, sodium tetraborate decahydrate and boric acid were supplied by Merck (Darmstadt, Germany).

Injection volumes were $100 \mu\text{l}$ of samples with ion concentrations above $100 \mu\text{g}/\text{l}$; levels under $100 \mu\text{g}/\text{l}$ required sample concentration. For trace enrichment a Waters IC-Pak A Anion concentrator ($8 \text{ mm} \times 5 \text{ mm I.D.}$, $2.16 \mu\text{equiv.}$) was used. Other conditions of this concentration were as follows: after a 2-min rinse of the preconcentrator system, the sample flowed through the concentrator column at $3 \text{ ml}/\text{min}$ for 4 min and was finally eluted in the last 0.5 min of the programme.

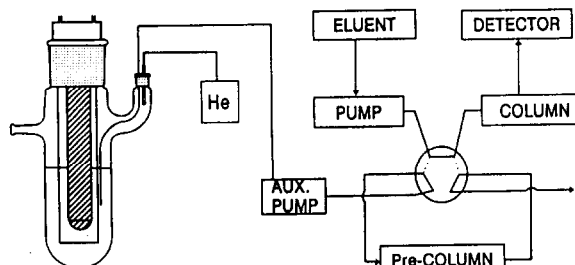


Fig. 1. Scheme of the overall assembly of the lamp and the chromatographic system.

Sample preparation

A 100-ml portion of resin was placed in a flask and 500 ml of ultrapure water obtained from a Milli-Q system (Millipore) were added. The mixture was stirred for 15 min and then filtered through an open column (50 cm × 3 cm I.D.). After placing 200 ml of the filtered liquid inside the lamp enclosure, the lamp vessel was closed and the air atmosphere was replaced with helium. An aliquot was analysed for anions by ion chromatography either by direct injection or using the preconcentrator. The water extract was irradiated for 60 min and chloride ions were determined a second time. The increase in chloride ions corresponds to the organochlorine content in the sample. All volumetric material used was prewashed several times with Milli-Q-purified water. Sodium chloride used in standards was obtained from Merck.

A sample of the same water used to prepare the resin extract was analysed as a blank. The chloride increase measured in the blank sample was subtracted from that obtained in the irradiated extract. At the same time this blank allowed the lamp container to be checked for possible contamination.

The initial chloride concentrations in the blanks were 3–5 $\mu\text{g/l}$ and the corresponding increase usually ranged from 5 to 10 $\mu\text{g/l}$. Samples irradiated in an open atmosphere gave larger chloride increases and their blanks showed lower repeatability, so in order to maintain the same inert conditions through the analysis, a helium atmosphere was used inside the lamp. Helium (quality 5.0) was supplied by Abelló (Barcelona, Spain).

Method validation

Owing to the origin of organochlorinate substances, no particular structure can be attributed to them and no specific analytical method can be applied. For this reason they were decomposed to inorganic chloride by UV irradiation and chloride ions were determined by ion chromatography. The purpose of this validation procedure was to monitor the decomposition and the subsequent increase in chloride ions after irradiation. It was also necessary to establish an irradiation

period that ensures the complete decomposition for the organochlorine substances.

The method was applied to solutions of organochlorine compounds of known structure. The sample solution was irradiated and analysed following the same procedure as described for sample preparation.

There are differences in decomposition according to the nature of the carbon atom to which the chloride ion is linked to in the organic molecule. The behaviour of aliphatic chlorine compounds towards UV irradiation differs from that of aromatic chlorine compounds. An aqueous solution of chloroethanol (Merck) and a solution of 2,6-dichlorophenol (Merck) were selected to represent aliphatic and aromatic compounds, respectively. For these substances the test was carried out at two levels of concentration, mg/l and $\mu\text{g/l}$.

The increase in chloride ion concentration after irradiation is shown in Figs. 2 and 3. Decomposition during the UV irradiation proved to be faster for samples of aliphatic than aromatic chlorine compounds. The results indicate that for low concentrations of organochlorine compounds in water ($\mu\text{g/l}$ level), decomposition was finished after 60 min of irradiation. This period was used for the resin tests. Although the organochlorine levels in resins may reach higher values they can be reduced after a resin treatment.

Application to anion-exchange resins

The concentration of chloride in anion-exchange resins produced by organochlorine compounds should not exceed 0.1 mg per litre of resin; this criterion is accepted as a resin specification [9].

After sample preparation, each extract was analysed for organochlorine content by ion chromatography. Owing to the high inorganic chloride levels in some resins, and knowing that in normal use the latter are regenerated and rinsed before use, the same treatments were applied to some resin samples. Subsequently the same method as described under *Sample preparation* was applied.

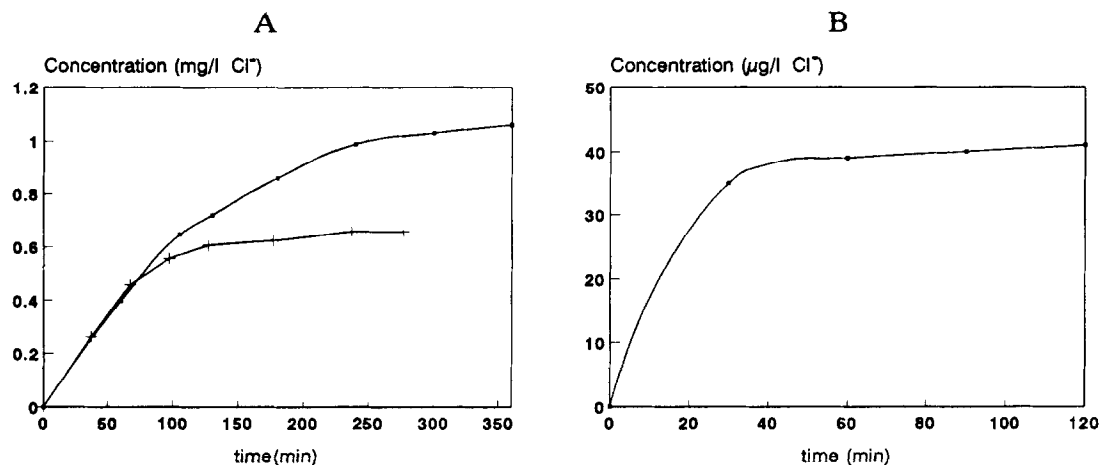


Fig. 2. Chloride concentration *versus* irradiation time of chloroethanol solutions at two concentration levels: (A) 2.4 mg/l (top curve) and 1.2 mg/l (bottom curve) of chloroethanol in Milli-Q-purified water; (B) 48 μg/l of chloroethanol in Milli-Q-purified water.

Regeneration method

This regeneration treatment was based on that used in power plants for resin regeneration, although modifications were made according to the resin volume employed. The method is as follows. A 100-ml portion of resin was placed in an open column and 500 ml of 2% NaOH (Merck) were poured through at a rate of 20 ml/min. After regeneration, the resin was rinsed with 5 l of Milli-Q-purified water at 40 ml/min.

The final conductivity and pH were tested in the last 100 ml of water (conductivity values should be <25 μS/cm).

RESULTS AND DISCUSSION

Table I gives the data obtained in each resin analysis.

The chromatograms in Fig. 4 correspond to a

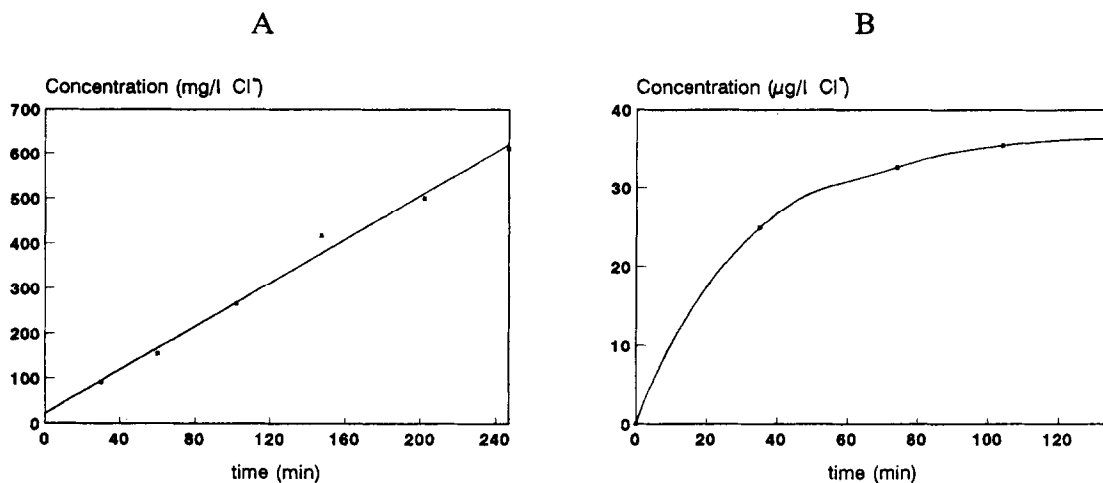


Fig. 3. Production of chloride with increasing irradiation time at different starting concentrations of 2,6-dichlorophenol. From a stock solution of 2,6-dichlorophenol (1050 mg/l in ethanol), dilutions were prepared using Milli-Q-purified water. (A) Solution of 2.3 mg/l of 2,6-dichlorophenol; (B) solution of 105 μg/l of 2,6-dichlorophenol.

TABLE I

RESIN ORGANOCHLORINE CONTENT EXPRESSED AS INCREASE IN ORGANIC CHLORIDE IN INDIVIDUAL SAMPLE EXTRACTS

Resin sample	Previous treatment	Cl ⁻ in extract (μg/l)		
		Before irradiation	After irradiation	Increase
1	None	2	4	2
2	None	1	3	2
3	None	12	14	2
4	None	7400	7800	400
	Rinsed with 5 l of water ^a	270	290	20
	Rinsed with 10 l of water ^a	110	170	60
	Regenerated	10	22	12
5	None	2800	3000	200
	Regenerated	17	65	48
6	Regenerated	16	452	436
7	Regenerated	69	541	472
	Regenerated	102	228	126
8	None	2300	—	—
	Regenerated	47	94	33

^a These samples were rinsed with the specified amounts of Milli-Q-purified water at a flow-rate of 20 ml/min with no previous regeneration.

water extract of one of the samples before and after irradiation.

Although detailed information on structure of the resin samples is not available, it is possible to summarize the available information as shown in Table II.

After rinsing with Milli-Q-purified water, the chloride concentration is decreased but regeneration proves to be more effective. The chloride levels both before and after irradiation in the water extract are more significantly reduced in the regenerated resin.

The chloride increase corresponds to the amount of organic chlorine in the resin. From the above results, it is possible to establish three different groups of resins according to their organic chloride content: (1) resins that do not need any treatment; the method can be applied directly to the supplied resin; these resins are described as nuclear grade and have undergone a

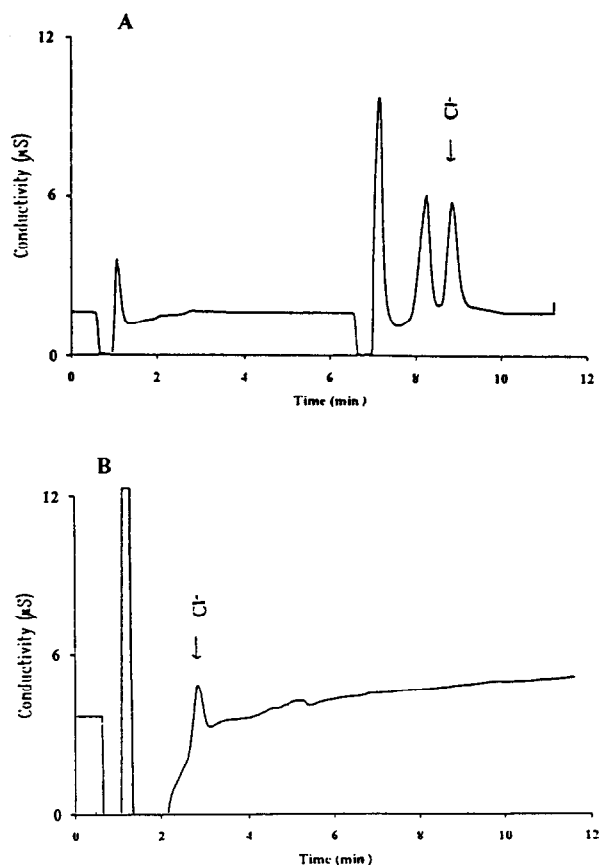


Fig. 4. Chromatograms of water extracts from resin (sample 7) after regeneration treatment and rinsing. (A) Analysis with sample pre-concentration; (B) the same water extract after 60 min of irradiation. Direct injection.

more thorough treatment during manufacture; (2) resins that initially show a high organochlorine content but in the water extract after

TABLE II
RESIN CHARACTERISTICS

Resin	Characteristics
1	Nuclear grade, strong exchange OH ⁻ resin
2	Nuclear grade, strong exchange OH ⁻ resin
3	Not available
4	Weak exchange, chlorinated amine salt
5	Weak exchange
6	Weak exchange
7	Strong exchange chlorinated amine salt
8	Not available

TABLE III
ORGANOCHLORINE CONTENT OF SEVERAL SAMPLES FROM THE SAME RESIN (NO. 7, TABLE II) AFTER REGENERATION AND RINSING

Extract No.	Cl ⁻ in extract (μg/l)		
	Before irradiation	After irradiation	Increase
1	102	228	126
2	112	411	291
3	67	367	273

regeneration this value decreases below 100 μg/l; and (3) resins that after regeneration show an increase exceeding 100 μg/l.

The whole process of regeneration, rinsing and irradiation of the water extract was carried out three times with samples of one of the resins (No. 7) and the results obtained are given in Table III. Each analysis was performed on a different day.

Specifications require chloride levels below 20

μg/l in the water extract. Considering this, we may conclude that resins 1–4 (after regeneration) were within the specifications.

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