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Electrodialytic sample treatment coupled on-line with column liquid chromatography for the determination of basic and acidic compounds in environmental samples

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ABSTRACT

The use of electrodialytic sample treatment coupled on-line with column liquid chromatography for environmental samples is described. The influence of the ionic strength on analyte recovery and the linearity and repeatability of the method were studied using anthraquinone-1,8-disulphonic acid and paraquat as model compounds. The completely automated procedure allows 10–20-fold selective enrichment of the analytes from 0.5–1.0-ml samples within 20 min. A group of sulphonic acids and the basic compounds paraquat and diquat were determined in ground and surface water samples.

INTRODUCTION

Dialysis is a well known technique for the separation of compounds of different molecular size. Coupled to column liquid chromatography (LC), dialysis can be used for on-line sample treatment [1–5]. In that case low-molecular-weight analytes diffuse through a high-molecular-weight cut-off membrane from the sample (donor) solution to an acceptor solution. However, if efficient and/or complete mass transfer in dialysis is required, dilution of the sample is inevitable. Consequently, a precolumn is needed to concentrate the analytes again before introduction into the LC system.

Electrodialytic sample treatment (EDIST) coupled on-line with LC is an alternative method for the isolation and enrichment of charged compounds from complex aqueous samples. The principle has been described recently [6]. The separation of analyte and matrix constituents is based on differences in molecular size and in electric charge. Transfer of analytes from the sample (donor) solution to the acceptor phase is achieved by both diffusion and electromigration. A laboratory-made block was used which contains various spacers and membranes which create donor, acceptor and electrode compartments. The donor and acceptor compartments (channels) are separated by a high-molecular-weight

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cut-off membrane (separation membrane). The flux, J, of (low-molecular-weight) analytes through the separation membrane is given by the Nernst–Planck equation:

$$J = J_{diff} + J_{migr} = -D\left(\frac{dC}{dx}\right) - \left(\frac{DCzF}{RT}\right)\left(\frac{dV}{dx}\right) \quad (1)$$

where J_{diff} and J_{migr} are the fluxes due to diffusion and migration, respectively, D is the diffusion coefficient of the analyte, x the coordinate perpendicular to the membrane, C the analyte concentration, z the valency of the analyte, F the Faraday constant, R the gas constant, T the temperature and dV/dx the electric field strength across the membrane.

When a voltage is applied to such a system, charged analyte molecules start to migrate from the donor to the acceptor phase (J_{migr}). As the concentration of the analyte in the acceptor phase increases, diffusion of analyte into the donor phase will occur; that is, J_{migr} will be counteracted by J_{diff}. When equilibrium has been reached ($J_{diff} = -J_{migr}$), the analyte concentration in the acceptor phase has reached its maximum value. In a previous study, with ephedrine as a model compound, 200 μl of sample could be treated in 10 min with a flowing donor and a stagnant acceptor phase, the enrichment being about tenfold. It was also shown that selective enrichment from blood plasma samples can be obtained. However, owing to the high conductivity of plasma, the enrichment was lower than that obtained with purely aqueous samples.

In this study, EDIST was used for the determination of basic and acidic compounds in ground and surface waters. Such samples usually have a lower ionic strength than biological samples, which should facilitate analyte enrichment. Further with the present automated EDIST system, larger sample volumes can be pretreated in the same time. Anthraquinone-1,8-disulphonic acid and several other sulphonic acids, which are used in different production processes, *e.g.*, for dyes and detergents, are often determined in river water. The sulphonic acids are usually determined by means of an ion-pair LC separation with UV detection at 220–230 nm because fluorescence detection is possible for only a few of them. Sample clean-up and enrichment are achieved by laborious off-line solid-phase extraction using an ion-pair reagent [7]. At the low UV wavelengths used, however, many interferences still show up in the chromatograms. The herbicides paraquat and diquat, which have found extensive industrial and domestic application as weedkillers, are used to study the determination of basic compounds in environmental samples. For their reversed-phase LC determination, complicated and time-consuming off-line sample treatment methods [8] are usually required because solid-phase enrichment of these strongly ionic compounds is difficult, especially if analysis has to be carried out at low-ppb levels.

EXPERIMENTAL

Chemicals

Acetonitrile, methanol, diethylamine, phosphoric acid, sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium chloride and phosphoric acid (85%) were purchased from J. T. Baker (Deventer, Netherlands). Hexanesulphonic acid was obtained from Eastman Kodak (Rochester, NY, USA) and tetrabutylammonium bromide from Aldrich Chemie (Steinheim, Germany). Anthraquinone-1,8-disulphonic acid was a gift from the Institute for Inland Water Management and Waste Water Treatment (RIZA, Lelystad, Netherlands), paraquat and diquat were from the National Institute of Public Health and Environmental Protection (RIVM, Bilthoven, Netherlands) and 1-amino-2-naphthol-4-sulphonic acid, *p*-toluenesulphonic acid and 4-nitrotoluene-2-sulphonic acid from Dr. W. Giger (Eidgenössische Anstalt für Wasserversorgung, Dübendorf, Switzerland). Paraquat solutions were prepared and stored in poly(vinyl chloride) vessels. Pooled Rhine water and pooled ground water samples were used without any further clean-up. The water sample from the river Rhine contaminated with anthraquinone-1,8-disulphonic acid was sampled by RIZA at Lobith on January 14th, 1991.

Chromatography

The LC system consisted of a Spectroflow 400 pump (Kratos, Ramsey, NJ, USA), a Spectroflow 757 UV detector and a 15 cm × 4.6 mm I.D. stainless-steel column packed with 5-μm RoSil C_{18} (Research Separation Labs., Eke, Belgium). The mobile phase for the paraquat and diquat analysis

consisted of 100 ml of acetonitrile, 900 ml of water, 3.64 g of hexanesulphonic acid, 10 ml of diethylamine and 16 ml of concentrated phosphoric acid, at a flow-rate of 0.7 ml/min. With the sulphonic acids, methanol–water (33:67, v/v) containing 1 m*M* tetrabutylammonium bromide and 0.02 *M* phosphate buffer (pH 6.5) was the LC eluent (flow-rate 0.8 ml/min). Peak areas and peak heights were measured with an HP 3396 A integrator (Hewlett-Packard, Waldbronn, Germany).

A Philips (Eindhoven, Netherlands) PW 9561 conductivity meter was used to measure the conductivity of the various sample solutions.

RESULTS AND DISCUSSION

Instrumental development

Electrodialysis block. The electrodialysis block consists of a set of spacers and membranes, held between two Perspex blocks which contain the electrode compartments (Fig. 1). Each compartment holds a coiled platinum wire electrode. Two extra spacers are used for mechanical support (not shown in Fig. 1). Ion-exchange membranes (Thomapor, Reichelt Chemie Technik, Heidelberg, Germany) are used to separate the acceptor and donor channels (equal volumes, each *ca.* 50 µl) from the electrode compartments. The donor and the acceptor phases are separated by a 10 000–15 000 molecular-weight cut-off membrane (Gilson, Villiers-le-Bel, France). The spacers of the EDIST block are made from PTFE sheets; PEEK (polyether ether ketone) tubing is used for the capillary connections.

The EDIST block is coupled on-line to an LC system by means of an automated six-port switching valve with a fixed injection loop. After electrodialytic treatment of the sample, the contents of the acceptor channel are transferred to the injection loop (volume 200 µl) by means of a syringe. This volume is acceptable, as band broadening is slightly reduced in the LC system by peak compression of the analytes in the usually aqueous injected zone on the top of the analytical column. Using a volume of 125 µl to transfer the contents of the acceptor channel (50 µl) to the injection loop, the highest recoveries (85%) were obtained. The same recoveries were obtained in experiments (data not shown here) where the EDIST block was replaced with a 50-µl loop, which means that the non-quantitative recovery is due to the incomplete transfer of the acceptor phase.

Compared with the EDIST block described in a previous paper [6], the new block has two major advantages. First, the *ca.* twofold larger volume of both the donor and acceptor channels of the new block allows the treatment of larger sample volumes. In order to obtain maximum recovery, a donor flow-rate of at best 25 µl/min could be used with the earlier block. In that event, the residence time of the analytes in the donor compartment (volume *ca.*

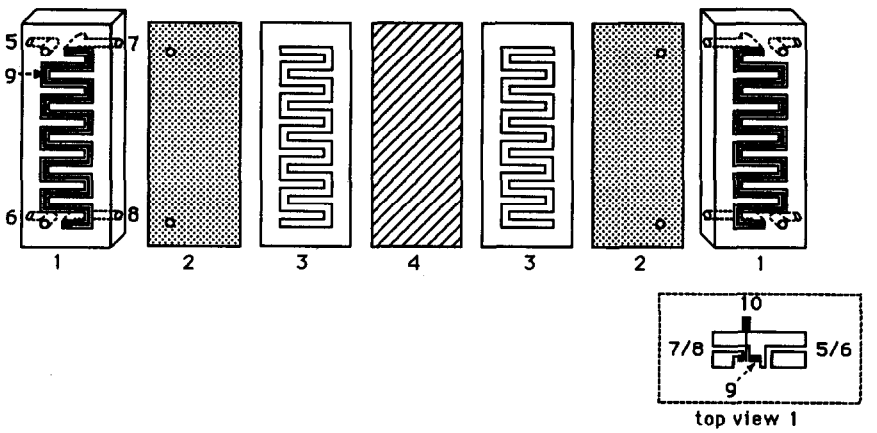

Fig. 1. Electrodialysis block. 1, Electrode vessel containing electrode compartment (meander); 2, ion-exchange membrane; 3, PTFE spacer with 50-µl flow channel; 4, separation membrane; 5, donor/acceptor outlet; 6, donor/acceptor inlet; 7, outlet electrode compartment; 8, inlet electrode compartment; 9, platinum electrode; 10, electrode connection.

20 μl) was *ca.* 1 min. For higher flow-rates the residence time was too short, which resulted in an incomplete recovery, *i.e.*, analyte was lost. In the present set-up, the volume of the donor compartment is *ca.* 50 μl and donor flow-rates of up to 50 μl/min can now be used. That is, the sample throughput is about twofold larger with the new block. Second, the electrode compartments of the present EDIST block are flushed continuously with an aqueous phosphate buffer at a flow-rate of *ca.* 1 ml/min. With the previous block only five or six electrodialysis experiments (10 min electrodialysis; 7.5 V) could be carried out without exhausting the buffer solution (0.1 *M* phosphate) [6]. With the present block, the continuous flushing of the electrode compartments with buffer solution prevents fouling and exhaustion of the buffer, that is, the number of experiments that can be performed without interruption is in principle limited only by the lifetime of the membranes.

With the basic drug ephedrine as a model compound, the influence of the electrode buffer concentration on analyte recovery was studied. Maximum recovery (*i.e.*, 85%) was obtained with 0.1–0.5 *M* phosphate buffer (pH 7). The use of 0.02 *M* phosphate buffer resulted in a decreased analyte recovery of only 30%. Probably the potential drop in the electrode compartments during electrodialysis was too high in the latter instance, causing a low electrical field strength in the acceptor and donor compartments and so a decreased J_{migr}. In all further work 0.1 *M* phosphate buffer solution (pH 7) was used to flush the electrode compartments.

EDIST set-up. The EDIST experiments were performed using a set-up similar to that described previously [6]. Fig. 2 shows the complete set-up. In this study, the EDIST procedure was fully automated by using an ASTED (Gilson) autosampler unit. Comparable results were obtained with two modified HP 1050 autosamplers (Hewlett-Packard), one for sample introduction and one for acceptor phase transfer.

In an EDIST run (coupled on-line to LC), several steps can be discerned (see Table I and Fig. 2). First, after loading the programme the donor pump (pump 1) flushes the EDIST unit with demineralized water and a reversed voltage is applied (reversed to the voltage applied during EDIST) in order to remove contaminants introduced during the previous run, from the separation membrane surface and the acceptor channel (PREP). Using this procedure, no clogging of the analytical system was observed during the lifetime of the membrane (*ca.* 200 analyses). After this flushing step, an automated syringe (syringe 1) injects sample into a sample loop which is attached to a six-port valve (sample valve) (LOAD).

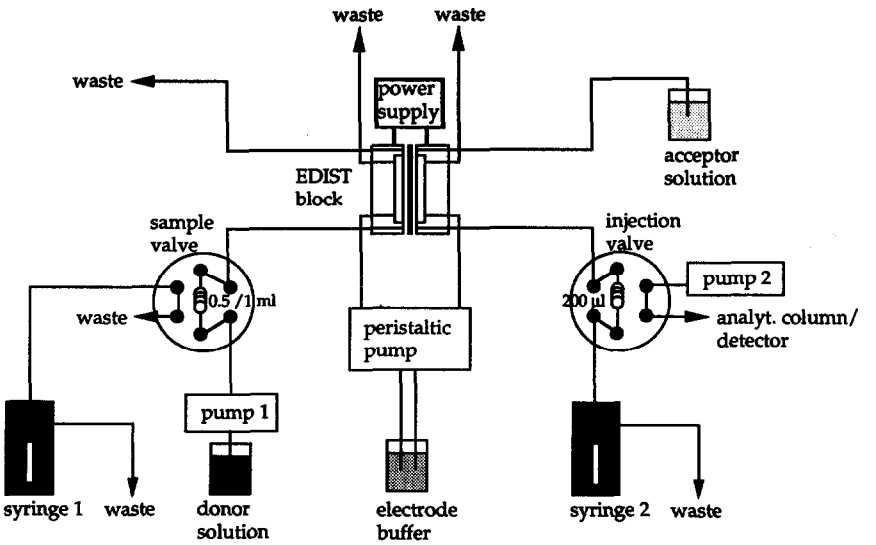

Fig. 2. Schematic set-up of the EDIST system with the sample valve and injection valve in the electrodialysis (ED) position.

TABLE I

TIME SCHEDULE FOR ELECTRODIALYTIC SAMPLE TREATMENT

Conditions: sample, 1.0 ml; donor flow-rate, 50 μl/min; acceptor, stagnant; electrodialysis time, 20 min.

Time (min)	Event	Step
0.0	Programme loading	
0.1	Pump 1 pumps donor solution; syringe 2 draws acceptor solution; reversed voltage on	PREP
3.0	Reversed voltage off; syringe 1 draws sample and injects sample in sample loop	LOAD
4.0	Sample valve switched; voltage applied	ED
24.0	Voltage switched off; acceptor phase drawn into injection loop	
24.1	Injection valve switched	ELUTE
25.0	End of run; start of next run	

Next, the sample valve is switched, the selected voltage is applied and the contents of the sample loop are flushed into the electrodialysis block by the donor pump (ED). After electrodialysis, a second automated syringe (syringe 2) transfers the contents of the acceptor channel to the injection loop which is attached to another six-port valve (injection valve). In the final step the injection loop is switched in-line between the LC pump (pump 2) and the analytical column and separation is performed (ELUTE). While one sample is being analysed, the next sample can be pretreated.

Determination of paraquat and diquat

If cationic compounds have to be determined, anion-exchange membranes are used to separate the electrode compartments from the acceptor/donor channels. If a voltage is applied only small anions will pass through the membrane, providing the electric current, while the cationic analytes will be retained in the acceptor phase.

During EDIST of a sample the analyte is enriched in the acceptor phase. This analyte enrichment can be expressed by means of the enrichment factor (*EF*) [6]:

$$EF = C_a/C_s \quad (2)$$

where C_a is the analyte concentration in the acceptor phase after (electro)dialysis and C_s is the initial analyte concentration in the sample (donor) solution. *EF* will be maximum when $J_{diff} = J_{migr}$ (see eqn. 1). Fig. 3 shows the dependence of *EF* for paraquat on the time of electrodialysis for two different donor flow-rates. The time of electrodialysis has been limited to 20 min because longer times would make the total time of analysis too long. As time increases more sample is introduced into the donor channel and more analyte will migrate to the acceptor channel. When a sample in 0.01 *M* phosphate buffer containing 0.01 *M* NaCl is used and the donor flow-rate is 50 μl/min, the equilibrium concentration in the acceptor solution is not reached within the time allotted. In other words, $|J_{diff}|$ still is smaller than $|J_{migr}|$. One way to increase *EF* is, of course, to increase the donor flow-rate. Fig. 3, however, shows that increasing the donor flow-rate from 50 to 100 μl/min does not cause a twofold increase in *EF* over the complete time interval. Probably the residence time of the sample in the donor channel is too short for complete analyte transfer from the donor to the acceptor phase. Small fluctuations in sample composition (ionic strength) may well cause irreproducible results under such conditions.

Since the electric field strength in the donor/acceptor solutions decreases with increasing ionic strength (the ionic strength in the electrode compartments being constant), the migration flux, J_{migr}, of the analyte from the donor phase to the acceptor phase and, therefore, the total flux, *J*, will be larger

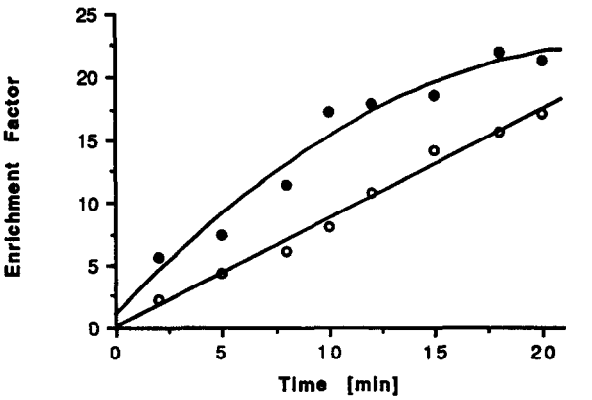

Fig. 3. Dependence of *EF* on the time of electrodialysis for a 1 ppm paraquat sample solution containing 0.01 *M* NaCl and 0.01 *M* phosphate buffer (pH 7). Donor flow-rate: (○) 50; (●) 100 μl/min. Voltage: 7.5 V. Each point represents the mean of two experiments.

TABLE II

DEPENDENCE OF RECOVERY OF PARAQUAT ON SAMPLE COMPOSITION

Sample (donor) flow-rate, 50 μl/min; $n = 2$; for further conditions, see text.

10 ppb paraquat solution in	Recovery (%)		Conductivity ($m\Omega^{-1}$)
	0.5 ml of solution	1.0 ml of solution	
0.01 *M* NaCl	57; 63	50; 70	1.1
0.02 *M* NaCl	56; 64	49; 71	2.3
0.05 *M* NaCl	50; 70	33; 47	5.2
Ground water	55; 65	48; 62	1.0

at low sample ionic strength. As the analyte is present, in most instances, in low concentration ($< 10^{-6}$ *M*), the ionic strength will mainly be determined by the matrix constituents. The influence of the ionic strength on analyte recovery is shown in Table II. For solutions with low conductivity (0.01 *M* NaCl), which are comparable to the ground water samples, 60% recovery is obtained for both 0.5- and 1.0-ml sample solutions. The highest recovery found for samples containing paraquat is 60%. This is lower than the 85% recovery found with the model compound ephedrine and with anthraquinone-1,8-disulphonic acid. The low recovery is possibly caused by sorption of paraquat to capillaries or compartment walls. This will lead to an incomplete transfer of the analyte from the acceptor

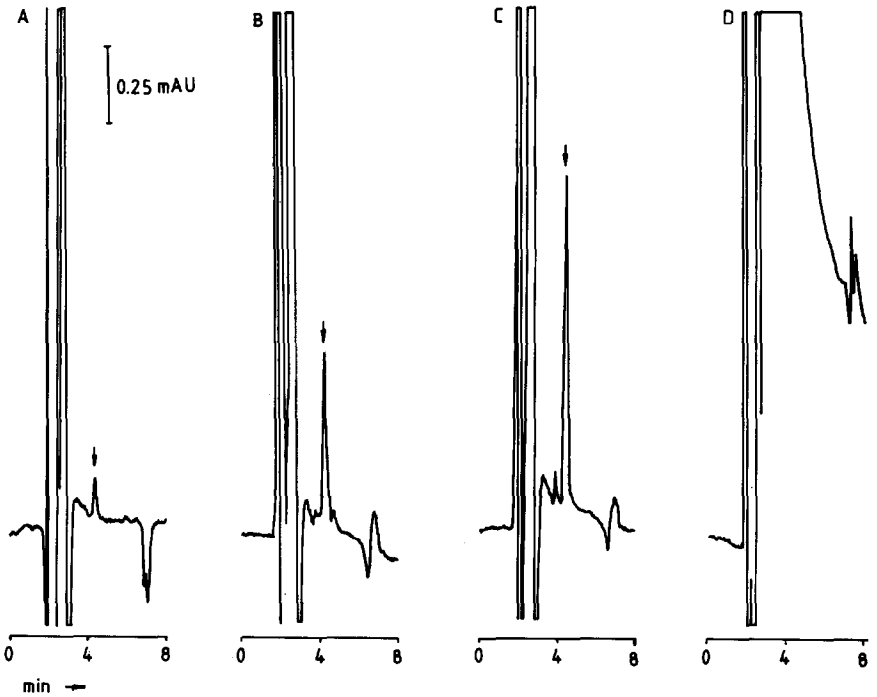

Fig. 4. LC–UV of ground water samples spiked with 10 ppb of paraquat. (A) 0.5-ml sample after dialysis (0 V); (B) 0.5-ml sample after EDIST (7.5 V); (C) 1.0-ml sample after EDIST (7.5 V); (D) direct injection of 200 μl of sample. For LC conditions, see text; UV detection at 254 nm. The arrow indicates the paraquat peak. Blank samples do not show a peak at the position of paraquat.

TABLE III

ANALYTICAL DATA FOR DETERMINATION OF PARAQUAT IN GROUND WATER

Parameter	Sample volume (ml)	
	0.5	1.0
Calibration plot (5–100 ppb)[a]	$y = 0.03 + 0.09x$	$y = -0.02 + 0.2x$
Regression coefficient (r^2)	0.996	0.992
R.S.D.[b] (%) ($n = 8$)	4	7
Detection limit (ppb) (S/N = 2)[c]	1	0.5

[a] y = Peak-height ratio; x = concentration.
[b] R.S.D. = Relative standard deviation.
[c] S/N = Signal-to-noise ratio.

channel to the injection loop. Increasing the ionic strength and, thus, the electric conductivity by a factor of two does not cause a decrease in recovery. At a fivefold higher ionic strength (0.05 *M* NaCl), however, a distinct loss is observed for sample volumes of 1.0 ml. At these high ionic strengths J_{migr} is smaller and an equilibrium between J_{diff} and J_{migr} is obtained, that is, plateau conditions are reached already for electrodialysis times of less than 20 min, *i.e.*, for sample volumes smaller than 1.0 ml. On prolonging the electrodialysis, no further enrichment of analyte will take place. For sample volumes of 0.5 ml the recovery is still 60%, indicating that after 10 min of electrodialysis plateau conditions obviously have not been reached.

LC–UV of spiked ground water samples with and without EDIST is shown in Fig. 4. Compared with the direct injection of ground water (Fig. 4D), the pretreatment by electrodialysis (Fig. 4B and C) shows its considerable advantage in terms of selectivity and enrichment. The enrichment which can be achieved by using EDIST is further demonstrated by comparing Fig. 4C and A, which shows a chromatogram obtained by dialysis (applied voltage 0 V; flowing donor, stagnant acceptor). Finally, it is interesting to compare the peak heights in Fig. 4B and C; obviously, 20-min EDIST of the paraquat-containing sample indeed yields twice the enrichment found after 10-min EDIST (5 ppb of paraquat; donor flow-rate 50 μl/min, stagnant acceptor; 7.5 V).

Data on the linearity (concentration range 5–100 ppb) and the repeatability of EDIST are given in Table III for 10 min (0.5 ml of sample) and 20 min (1.0 ml of sample) of sample treatment. As is to be expected, the slope of the plot for 1.0 ml of sample is about twice as large as that for 0.5 ml of sample. With the present set-up the detection limit for paraquat is 0.5 ppb. With pretreatment methods for ground water samples involving the use of pre-

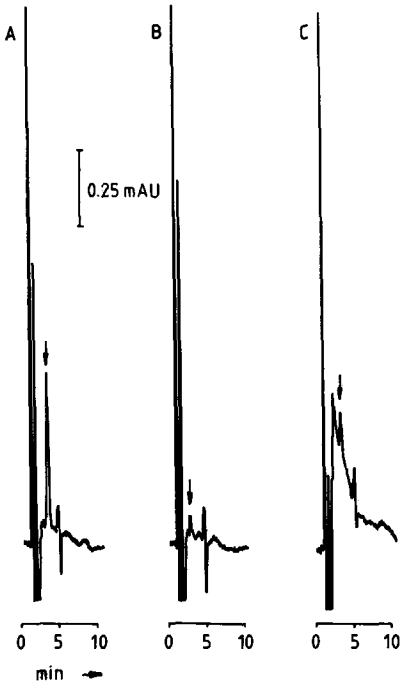

Fig. 5. LC–UV of ground water samples spiked with 10 ppb of diquat. (A) 1.0-ml sample after EDIST (7.5 V); (B) 0.5-ml sample after dialysis (0 V); (C) direct injection of 200 μl of sample. For LC conditions, see text; UV detection at 310 nm. The arrow indicates the diquat peak. Blank samples do not show a peak at the position of diquat.

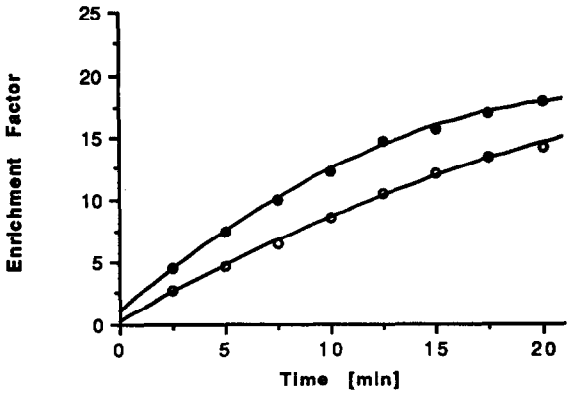

Fig. 6. Dependence of *EF* on the time of electrodialysis for a 1 ppm ADS sample solution containing 0.01 *M* NaCl and 0.01 *M* phosphate buffer (pH 7). Donor flow-rate: (○) 50; (●) 100 μl/min. Voltage: 7.5 V. Each point represents the mean of two experiments.

columns, irreproducible results are generally obtained even at 10–20-fold higher concentration levels [9]. In addition, these methods, which usually are off-line, are difficult to automate.

Fig. 5 shows the LC–UV determination of diquat in ground water using (A) EDIST, (B) conventional dialysis and (C) a direct injection of 200 μl of ground water. As the optimum detection wavelength for diquat is 310 nm, which is a more selective wavelength than the 254 nm used with paraquat, the direct-injection chromatogram shows less interferences. The selectivity gain is, however, still obvious and the enrichment due to EDIST is clearly demonstrated by comparing Fig. 5A and B.

Determination of sulphonic acids

For EDIST of acidic compounds, cation-exchange membranes have to be used to prevent migration of the anionic analytes into the electrode compartments. The dependence of *EF* for anthraquinone-1,8-disulphonic acid (ADS) on the time of electrodialysis for two donor flow-rates is shown in Fig. 6. It is evident, as with paraquat, that although *EF* increases, the recovery decreases at higher donor flow-rates. Table IV shows data on analyte recovery as a function of the ionic strength of the sample solution. Apart from the higher maximum recovery (85% *vs.* 60%; see above), the results are closely similar to those found with paraquat. Substantial losses start to occur for 0.05 *M* NaCl solutions and relatively large, *i.e.*, 1.0-ml, sample solutions, indicating that plateau conditions are reached.

Analytical data on the linearity (concentration range 5–100 ppb) and the repeatability of the determination of ADS in river Rhine water are shown in Table V. The detection limit of *ca.* 2 ppb is essentially the same as that reported using off-line solid-phase extraction [7]. The main advantage of EDIST is, of course, the automation potential.

LC–UV of spiked Rhine water samples is shown in Fig. 7. The accuracy of the method is demonstrated by the equal height of the ADS peaks obtained after 10-min EDIST of a 0.5-ml sample containing 20 ppb of ADS (Fig. 7A) and 20-min EDIST of a 1.0-ml sample containing 10 ppb of ADS (Fig. 7B). The number of interferences in the chromatogram is larger than with the paraquat samples. Probably negatively charged low-molecular-weight humic and fulvic acids, which are pres-

TABLE IV

DEPENDENCE OF RECOVERY OF ANTHRAQUINONE-1,8- DISULPHONIC ACID ON SAMPLE COMPOSITION

Sample (donor) flow-rate, 50 μl/min; $n = 2$; for further conditions, see text.

10 ppb ADS sample solution in	Recovery (%)		Conductivity ($m\Omega^{-1}$)
	0.5 ml of solution	1.0 ml of solution	
0.01 *M* NaCl	83; 87	82; 88	1.1
0.02 *M* NaCl	83; 87	79; 91	2.3
0.05 *M* NaCl	83; 87	50; 60	5.2
Rhine water	83; 87	81; 89	1.1

TABLE V

ANALYTICAL DATA FOR DETERMINATION OF ANTHRAQUINONE-1,8-DISULPHONIC ACID IN RIVER RHINE WATER

Parameter	Sample volume (ml)	
	0.5	1.0
Calibration plot (5–100 ppb)[a]	$y = -0.02 + 0.02x$	$y = 0.21 + 0.04x$
Regression coefficient (r^2)	0.997	0.996
R.S.D. (%) ($n = 8$)	5	3
Detection limit (ppb) (S/N = 2)	2.5	1.5

[a] y = Peak-height ratio; x = concentration.

ent in large amounts in river Rhine water, are transferred to the acceptor phase together with ADS. This explanation is supported by the fact that the interfering peaks in the chromatogram are larger when a 1.0-ml instead of a 0.5-ml sample is analysed (Fig. 7B *vs.* Fig. 7A). With the positively charged paraquat, the humic and fulvic acids of course migrate in the opposite direction and will not reach the acceptor phase. Nevertheless, comparison with the chromatogram from direct injection of a spiked Rhine water sample (Fig. 7D) adequately illustrates the potential of EDIST.

The determination of ADS in a real sample is shown in Fig. 7C. The sample was taken from the river Rhine at Lobith on January 14th, 1991. Analyses of a number of water samples from the same river (December 1990–January 1991) performed by the RIVM showed the presence of ADS in

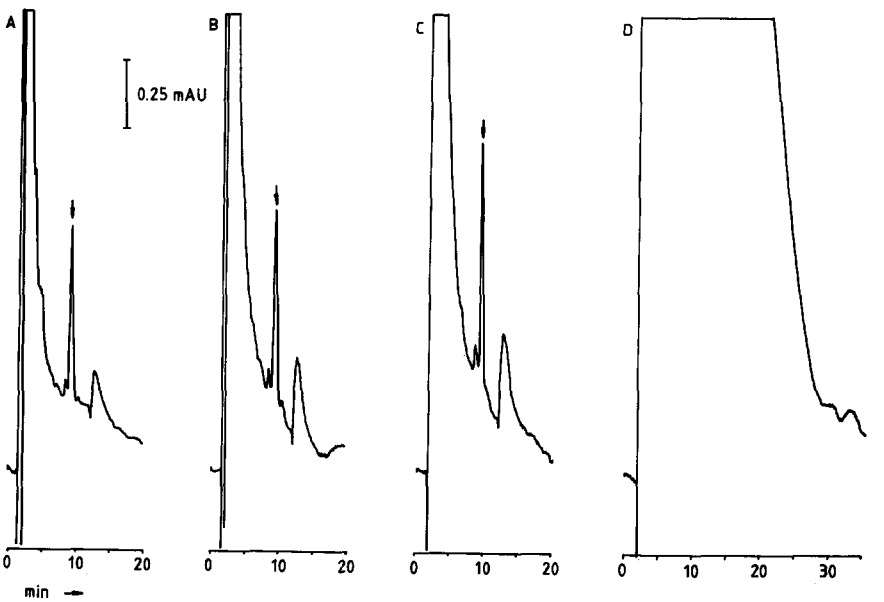

Fig. 7. LC–UV of ADS-spiked Rhine water samples after EDIST (7.5 V). (A) 0.5-ml sample spiked with 20 ppb; (B) 1.0-ml sample spiked with 10 ppb; (C) 1.0-ml sample taken at Lobith (January 14th, 1991). For comparison: (D) direct injection of 200 μl of Rhine water spiked with 10 ppb. For LC conditions, see text; UV detection at 254 nm. The arrow indicates the ADS peak. Blank samples do not show a peak at the position of ADS.

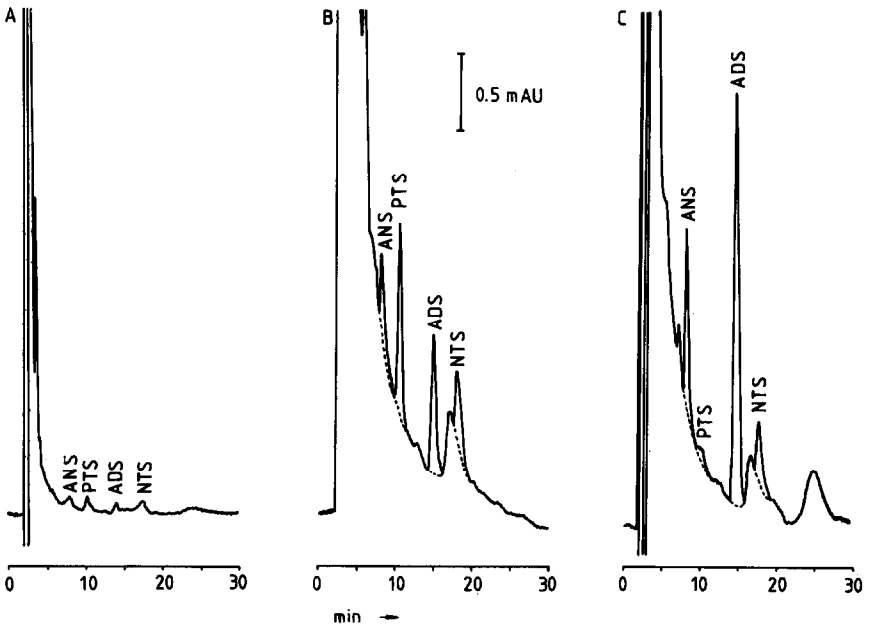

Fig. 8. LC–UV of Rhine water spiked with 50 ppb of a mixture of four sulphonic acids: 1-amino-2-naphthol-4-sulphonic acid (ANS), *p*-toluenesulphonic acid (PTS), anthraquinone-1,8-disulphonic acid (ADS) and 4-nitrotoluene-2-sulphonic acid (NTS). (A) Dialysis of 1.0-ml sample; (B) EDIST (7.5 V) of 1.0-ml sample, UV detection at 230 nm; (C) EDIST (7.5 V) of 1.0-ml sample, UV detection at 254 nm. Dashed lines, blank run. For LC conditions, see text.

the river water at that time, probably as the result of an accidental spill. The concentration levels determined using solid-phase extraction were comparable to that found by us in the sample shown in Fig. 7C (14 ppb).

As a further illustration of the potential and limitations of on-line EDIST and LC–UV, Fig. 8 shows the analysis of a mixture of four sulphonic acids. Compared with conventional dialysis (Fig. 8A), EDIST effects an enrichment of the negatively charged analytes (Fig. 8B); the gain in selectivity, however, is unsatisfactory. For two compounds, ADS and amino-2-naphthol-4-sulphonic acid, both the selectivity and sensitivity could be improved considerably by changing the detection wavelength from 230 to 254 nm (Fig. 8C).

CONCLUSIONS

EDIST is an effective sample treatment method for the clean-up and enrichment of anionic and cationic analytes from river and ground water samples prior to LC. The on-line coupling to LC is easy to automate, which makes the method suitable for routine analysis. EDIST can be used as a fast screening method at low concentration levels; it displays good linearity and repeatability. The method is especially suited for the determination of basic compounds in environmental samples. When determining acidic compounds, humic and fulvic acids appear to interfere to some extent. Further study is required in this area, using for instance other types of membranes, *e.g.*, with a lower molecular-weight cut-off.

The low ionic strength of environmental water samples allows enrichment factors of up to 20 to be obtained. With the present EDIST unit, sample volumes of *ca.* 1 ml can be treated within 20 min (Fig. 3). The on-line combination of EDIST with other sample treatment methods, such as solid-phase extraction, may well allow the treatment of larger sample volumes in order to obtain the low detection limits often required in trace analysis. Current research is devoted to this area, and also to the optimization of EDIST for the treatment of biological fluids, with which enrichment factors of up to 10 have already been realized.

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