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AUTOMATED DUAL COLUMN COUPLED SYSTEM FOR SIMULTANEOUS DETERMINATION OF CARBOXYLIC ACIDS AND INORGANIC ANIONS

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SUMMARY

Isocratic anion-exchange separations have often been found inadequate for mixtures of carboxylic acids with weakly and strongly retained inorganic anions. In the coupled column approach, separating performance is improved by the simultaneous use of two separation modes. After an injection onto an ion-exclusion column all anions of strong acids elute in a narrow zone close to the dead volume and are easily diverted to an anion-exchange system for an interference free separation. Carboxylic and other relatively weak organic or inorganic acids are separated by ion exclusion and are thus removed as interferences in the separation of anions by anion exchange. A simple and reliable preconcentration technique has also been developed, allowing a simultaneous trace enrichment of weak and strong anions prior to their injection on the coupled system.

INTRODUCTION

In highly purified water as it is used in power plants and in semiconductor manufacturing, trace concentrations of carboxylic acids and inorganic anions are usually narrowly specified[1]. If the acceptable levels are exceeded, different removal techniques have to be employed for inorganic anions and for organic acids. Since both types of contamination frequently occur in the same time, it becomes important for the operating personnel to be able to distinguish between the organic and inorganic contamination levels. Ion chromatography has gained a broad acceptance as a tool for analyzing low levels of inorganic ions in water samples[2–4].

Yet, a simultaneous determination of short-chain carboxylic acids in mixtures with the monovalent inorganic anions such as fluoride, chloride, carbonate and bromide still represents a difficult separation problem even with the most recently introduced high-efficiency anion-exchange columns[4].

Such inherent limitations of (mono-dimensional) anion-exchange chromatography are explainable with the help of a theoretical framework developed by Giddings[5–7]. This author has derived a fundamental relationship between the maximum number of peaks that can be resolved (peak capacity n) and the column

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efficiency as measured by the number of theoretical plates (N):

$$n = 1 + \tfrac{1}{4}[N^{1/2}\ln(V_x/V_0)] \quad (1)$$

where V_0 and V_x signify the initial and final volume of an available retention range on any given chromatographic column. Due to the characteristic peak grouping peculiar to anion-exchange separations a typical elution range ratio for the seven anions in question (fluoride, chloride, carbonate, bromide, formate, acetate and propionate) is $V_x/V_0 = 3$. Assuming $N = 3000$, the corresponding maximum peak capacity can be calculated by eqn. 1 as $n = 16$. Theory shows[7] that the number of fully resolved, randomly distributed single component peaks n_r never exceedes 18% of n, resulting in only about three fully resolvable peaks in an area "crowded" by seven or more anionic species. Under isocratic conditions attempts to extend the elution range lead to an excessively large or permanent retention for phosphate and sulfate. The resulting loss of information is considered unacceptable by the analysts in the power and semiconductor industries[4]. A promising approach to the problem appears to be offered by the newly introduced gradient techniques for single column[8] and suppressed ion chromatography[9]. In this report we describe yet another approach —an increase in resolving power that can be achieved by the coupling of two separation modes (ion exclusion and anion exchange)— in a single chromatographic system.

EXPERIMENTAL

Instrumentation

The liquid chromatographic system consisted of two Waters (Milford, MA, U.S.A.) Model 590 programmable pumps and two Model 430 conductivity detectors. Both chromatographic pumps were equipped with the high sensitivity accessories (pulse damping) and the event boxes (interfaces between the pumps and controlled external devices such as switching valves or preconcentration pumps) obtainable from the same supplier.

Four of Waters automatic column switching valves were used for changing the configuration of the system and for manual or automatic injection as determined by the program stored in one of the two programmable pumps. A trace enrichment module (Waters PN 07448) containing a single piston pump and a holder for preconcentration cartridges (Guard Pak Assembly ILC, Waters PN 33100) was also controlled by the same program through the event box interface. The anion-exchange and ion-exclusion columns were as described in our previous publication[10]. IC Pak anion concentrator cartridges (5 × 8 mm, Waters PN 07358) containing polyacrylate based anion-exchange resin of approximately same mequiv./g capacity as in the anion-exchange column were utilized for preconcentration of samples. Data acquisition was carried out with the help of a Model 840 data station and two SIM interfaces. Collection of chromatographic data was initiated by a signal connection via the event box.

Eluent preparation for system one (ion exclusion)

A 10 mM concentrate of 1-octanesulfonic acid was prepared first. An amount of 2.163 g of the sodium salt of octanesulfonic acid (98%, Aldrich 22, 156-2) purified by

crystallization was placed into a 250-ml beaker and dissolved in 100 ml of Milli-Q (Millipore, Bedford, MA, U.S.A.) water using a magnetic stirrer. A 100-ml volume of a precleaned cation-exchange resin was than added to this solution and the resulting slurry was stirred for *ca.* 10 min. In the next step the cation-exchange resin was removed from the solution by filtration through a prewashed (10 ml water) 0.45-μm filter (Type HA, Millipore). Proper care had to be taken that the resin inside the filter funnel was wet throughout the whole filtration. This ensured that the octanesulfonic acid was quantitatively transferred into the filtrate. In order to keep the resin covered with solution and to wash out the sulfonic acid as completely as possible *ca.* 800 ml of Milli-Q water had to be added from a clean container and prepared before the actual filtration began. The resulting *ca.* 900 ml of filtrate were transferred into a volumetric flask and filled up to 1000 ml. This 10 m*M* octanesulfonic acid solution was stable for up to one month.

The 1 m*M* eluent was than prepared freshly by diluting aliquots of the concentrate and by filtration through a Millipore HA 0.45-μm filter. The observed background conductance of such clean ion-exclusion eluent was in the range of 320 to 330 μS. The pH of the eluent was *ca.* 3.0 which led to an useful retention behavior for all acids with pK_a values of 3 or greater.

Eluent preparation for system two (anion exchange)

A 0.649-g amount of 1-octanesulfonic acid, sodium salt was dissolved in 1 l of Milli-Q water in a volumetric flask. Filtration and degassing with the help of 0.45-μm Millipore HA filters followed. Resulting solution was 3 m*M* in sodium octanesulfonate. It was found that interferences by chromatographic peaks stemming from impurities could be kept at a minimum, if both the sodium salt and the prepared sulfonic acid were from the identical batch and from the same manufacturer.

Sample preparation

Samples were collected in 200-ml polystyrene tissue culture flasks (Corning Glass Works, Corning, NY, U.S.A.) (PN 25115). These particular flasks were chosen after a long term evaluation of possible sample containers from several different manufacturers. It was found that all other containers except the ones recommended here, contributed traces of anions at concentrations above the detection limits of our method. Prior to sample collection the tissue culture flasks were rinsed five times to overflowing with Milli-Q water as well as soaked for 24 h filled with the same ultrapure water. The samples were drawn into the system through a PTFE tubing immersed in the flask and connected to a trace enrichment pump (TEP in Fig. 1) at the other end. Additional steps that are discussed in the Results and Discussion section of this article were required for highly alkaline samples and for samples with high concentration of boric acid.

Standard solutions

All standard mixtures were prepared by a dilution of 1000-ppm stock solutions containing a single anion. Weighed amounts of salts rather than acids were used for the preparation of stock solutions. Concentrates of 1000 ppm of anions of carboxylic acids were found stable for at least six weeks. No measurable changes of concentrations of stock solutions of inorganic acids were found during a time period lasting twelve

months. The Milli-Q water and polypropylene containers (Nalge, Rochester, NY, U.S.A.) (PN 4000) were utilized for all standards in the ppm range of concentrations. The tissue culture flasks were used for standards containing less than 500 ppb[a] of a single anion. All standards containing less than 50 ppm of any anion were prepared freshly for each of the experiments.

System operation

The system schematics illustrated in Fig. 1 could be used for both, manual injection of mixtures at higher concentrations (*ca.* 1 ppm and more) and for automatic preconcentration at sub-ppm levels. Each of the four six-port high-pressure switching valves (TEV, 1TV, 2TV and MIV in Fig. 1) fulfills a different function within the coupled system. The trace enrichment valve (TEV) switches the trace enrichment cartridge (CON) from the sample line to the flow of the eluent coming either from pump 1 or from pump 2 as determined by the position of the first transfer valve (1TV). The second transfer valve (2TV) provides the necessary link between the two systems

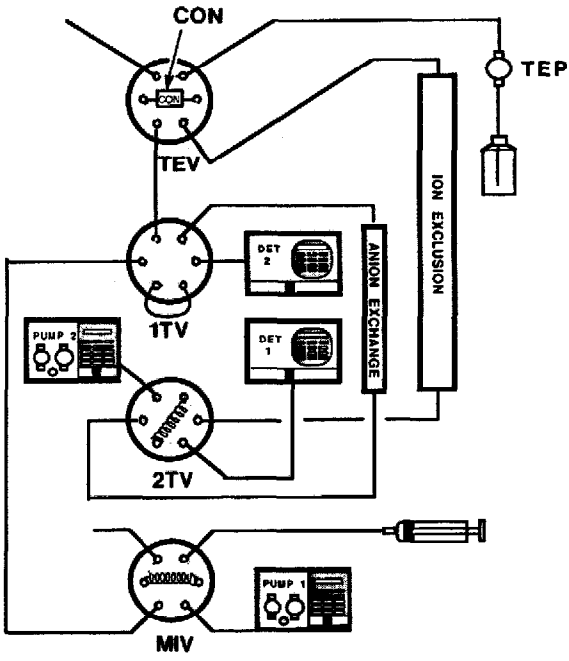


Fig. 1. General configuration of the coupled ion-exclusion–anion-exchange system. Pump 1 and detector 1 (DET 1) are used in conjunction with the ion-exclusion column. Pump 2 and detector 2 are parts of the anion-exchange system. TEP = Single piston trace enrichment pump; CON = precolumn used for trace enrichment; TEV = high-pressure switching valve utilized for connecting the precolumn into the sample stream for a known period of time; 1TV = first transfer valve connecting both pumps to the precolumn; 2TV = second transfer valve which makes it possible to transfer fractions of the ion-exclusion column eluate to the anion-exchange column; MIV = manual injection valve used for sample introduction in cases that do not require preconcentration (ppm range).

[a] Throughout this article the American billion (10^9) is meant.

TABLE I

PROGRAM FOR THE FRACTION TRANSFER BETWEEN TWO SYSTEMS (MANUAL INJECTION)

Refer to Fig. 2 for the positions of the second transfer valve (2TV) controlled by the events 5 and 6. Events 1–4 and 7 have been assigned to various functions of the sample preconcentration procedure explained in Table II and in Fig.3.

Step No.	*Time (min)*	*Events*			*Description*
		5	*6*	*8*	
1	–	N	F	F	Loading the sample into the sample loop of the manual injection valve. N = on, F = off signifying two different levels of voltage on one of the eight pairs of contacts (8 events) in the M590 event box
2	0	N	F	F	Manual injection onto the ion-exclusion column. Data acquisition by system 1 is activated by a direct signal connection between the manual injector and the system interface (SIM)
3	4.5	F	N	P	Transfer of 500 μl from the ion-exclusion separation to the anion-exchange column. A signal pulse P (event 8) starts the data acquisition on system 2
4	25.0	N	F	F	2TV returns to its original position separating the two systems

for the transfer of a fraction of the void volume from the ion-exclusion separation onto the anion-exchange column. The appropriate time sequence of column switching steps by valves 1TV, 2TV and TEV is determined by a program written and stored in the microprocessor of one of the two programmable chromatographic pumps. Detailed descriptions of such programs are given in Tables I and II. The only column switching valve that is actuated manually outside the control of an automatic program is the

TABLE II

PROGRAM FOR THE FRACTION TRANSFER BETWEEN TWO SYSTEMS (WITH SAMPLE PRECONCENTRATION)

Refer to Fig. 3 for the positions of the valves controlled by the events 1–6. TEV, events 1 and 2; 1TV, events 3 and 4; 2TV, events 5 and 6; TEP, event 7. Data acquisition for both separations, event 8. N = on, F = off.

Step No.	*Time (min)*	*Events*								*Description*
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	
1	0.0	F	N	N	F	N	F	F	F	Equilibrate precolumn
2	2.0	N	F	N	F	N	F	N	F	Load sample
3	12.0	F	N	F	N	N	F	N	P	Inject part 1
4	12.5	F	N	N	F	N	F	F	F	Inject part 2
5	13.0	N	F	N	F	N	F	F	F	End injection
6	16.5	N	F	N	F	F	N	F	F	Transfer
7	36.5	N	F	N	F	N	F	F	F	Reset valves

manual injection valve (MIV). A signal connection between the MIV and the system interface module (SIM) of the system 1 starts the recording of the ion-exclusion separation in the same instant as the MIV is turned from the load position to the inject position (from step 1 to step 2 in Fig. 2). Another signal connection (MIV to M590 event box) starts the timer for the automatic program sequence (steps 2, 3 and 4). The data acquisition for the anion-exchange separation is then initated simultaneously with the actuation of the 2TV (step 3 in Table I and in Fig. 2).

The positions of the valves TEV and 1TV remain unchanged during the entire manual injection procedure (see Fig. 2) and are therefore not listed in Table I.

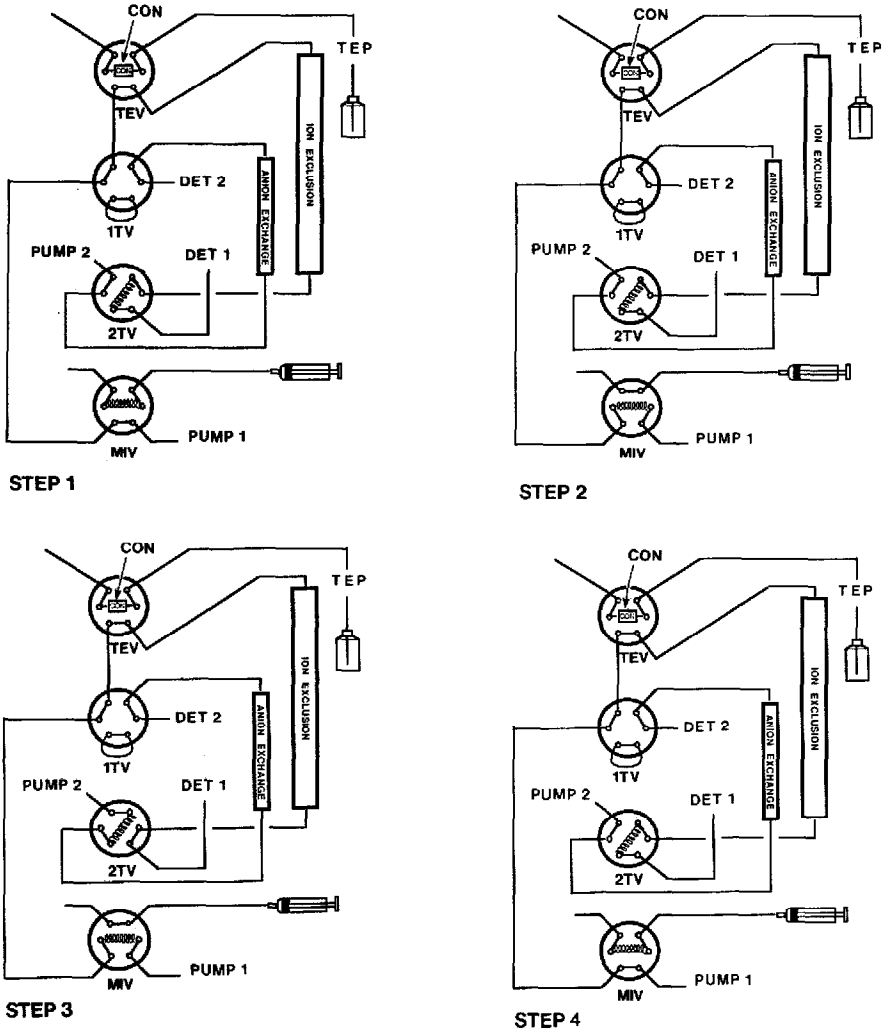


Fig. 2. Column coupling at relatively high concentrations (ppm range). Refer to the description presented in the Experimental section and to the program given in Table I. step 1 = Manually load sample into loop via syringe; step 2 = manual injection into system 1; step 3 = transfer void volume from system 1 to system 2; step 4 = transfer valve returns to the original position, the two systems are separated again.

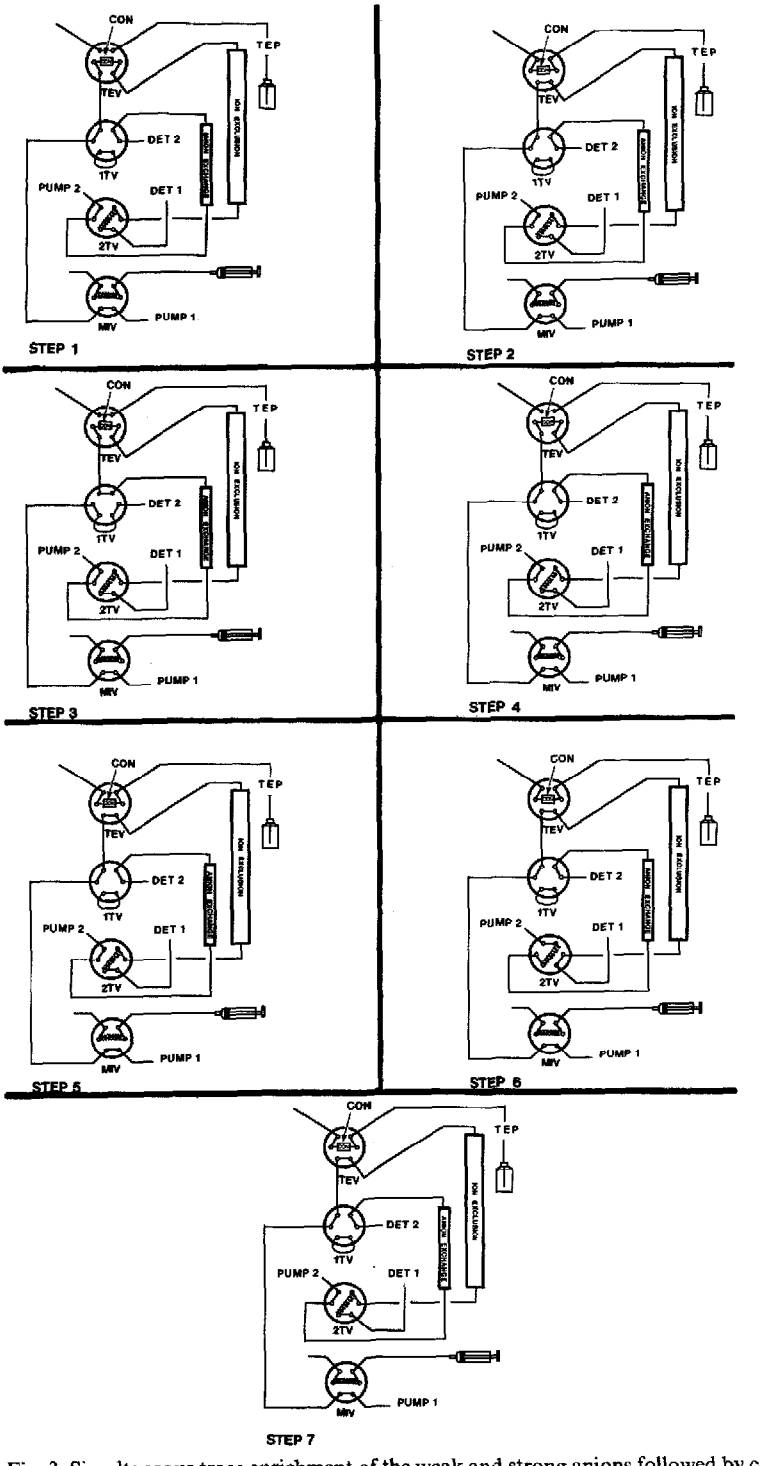


Fig. 3. Simultaneous trace enrichment of the weak and strong anions followed by concurrent ion-exclusion and anion-exchange separations. Table II describes the details of the column switching program. Additional description is offered in the Experimental section. Step 1 = Purge sample line/equilibrate concentrator/TEP on; step 2 = load sample onto concentrator/TEP on; step 3 = inject sample with eluent 2/TEP off; step 4 = inject sample with eluent 1; step 5 = end of injection; step 6 = transfer void volume to system 2; step 7 = reset valves to the initial position.

During a procedure utilizing trace enrichment on a precolumn mounted on the TEV it is the position of the MIV that remains unchanged (see Fig. 3). Injection of a sample is achieved by positioning the precolumn (CON) into the eluent stream. Such an injection is then a part of a fully automatic sequence an example of which is given by Table II. In the automatic procedure the data acquisition is initiated simultaneously for both chromatographic systems by step 4 in Table II. The real retention time for the second system (anion exchange) is than calculated by subtracting the time difference between steps 7 and 4 in Table II from the apparent retention time obtained in the recording. As an alternative, a synchronous program with the one in pump 1 (see Table II) can be run inside pump 2 containing only one segment providing a pulsed output at the time of step 7. By connecting SIM 1 to the event box of pump 1 and with a connection between SIM 2 and the event box 2, real retention times can be recorded for both systems.

RESULTS AND DISCUSSION

Limitations of anion-exchange separations

As predicted by theory (see Introduction), the anion-exchange separation mode is inherently inadequate whenever mixtures of carboxylic acids and early eluting inorganic anions are to be separated. To illustrate the phenomena we have attempted a separation of thirteen organic and inorganic anions (Fig. 4). Note that while the chosen anion-exchange column efficiently separates the six late eluting anions (peaks 8–13 in Fig. 4), a lack of selectivity and separation efficiency is observed for the initial seven peaks of some of the inorganic anions and of all organic acids present in the sample. Furthermore, the initial peak of the seven coeluting anions could easily be mistaken for a signal corresponding to a larger concentration of just a single anion (*i.e.*, fluoride).

Coupling of ion exclusion and anion exchange

In an earlier work[10] we have successfully applied column coupling to simultaneous separations of traces of inorganic anions in the presence of large concentra-

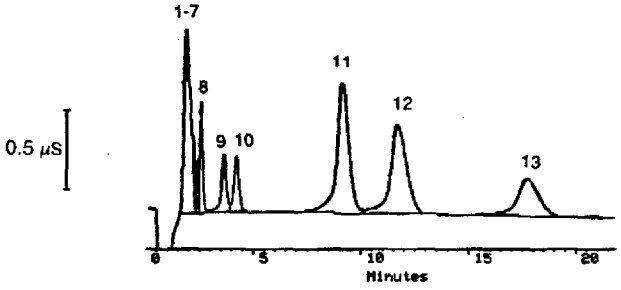


Fig. 4. Attempted anion-exchange separation of a mixture of thirteen organic and inorganic anions. Conditions: column, Waters IC PAK Anion (5 × 0.46 cm I.D.); eluent, 3 m*M* sodium octanesulfonate; flow-rate, 1 ml/min; sample, 100 μl of a mixture of thirteen anions; detection, Waters M430 conductivity detector. Anions: 1 = fluoride (0.5 ppm); 2 = glycolate (2.0 ppm); 3 = formate (1.0 ppm); 4 = acetate (10.0 ppm); 5 = propionate (20.0 ppm); 6 = butyrate (20.0 ppm); 7 = iodate (50.0 ppm); 8 = chloride (1.0 ppm); 9 = bromide (2.0 ppm); 10 = nitrate (2.0 ppm); 11 = iodide (20.0 ppm); 12 = sulfate (2.0 ppm); 13 = thiocyanate (5.0 ppm).

tions of boric acid. Use was made of the fact that on an ion-exclusion column all strongly acidic anions elute within the dead volume, while only the weak acids, as for example the boric and carbonic acid, are retained and separated. In order to broaden the scope of the technique and to make it applicable to a larger variety of weak and strong acids we have now carried out a more detailed investigation of the dead volume zone of an ion-exclusion separation.

The mixture of anions for our experiments with fraction transfer from ion exclusion to anion exchange consisted of two anions of weak acids (fluoride and phosphate) and of three anions belonging to strong acids (chloride, bromide and nitrate). The ion-exclusion chromatogram resulting from an injection of such a mixture is shown in Fig. 5. In this separation four of the chosen anions coelute with a strongly negative signal caused by water from the injected sample and do not appear in the form of distinct chromatographic peaks if conductivity is utilized as a detection mode. The width of the fluoride peak was used to estimate the optimum size of the fraction cuts from the ion-exclusion separation for the transfer to the anion-exchange column. To prevent fraction splitting it is recommended[7] not to exceed the size of about 4σ of an average peak for any given separation. Based on these considerations 500 μl were chosen for a fraction volume. The perceived end point of the negative deflection marking the dead volume was chosen as a center with the experimental fractionation range reaching an equal distance in both directions (see Fig. 5).

As seen from Figs. 6 and 7, anions of strong acids are concentrated in fraction 1. Their recoveries from that cut after the transfer to the anion-exchange column are in excess of 90%. On the other hand, the investigated fractionation procedure fails for the anions of weak acids. The recoveries for fluoride remain low throughout the whole range between 4 and 6 min. Because of such strong retention, ion exclusion becomes clearly the preferred separation mode for fluoride in the coupled systems. The bulk of the phosphate concentration was found to be located at the boundary between fractions 1 and 2. The recoveries for phosphate were split almost equally between these two fractions. To improve the results for this anion fraction cut 1 could be shifted by about 250 μl toward the larger retention volumes. However, such change would sharply decrease the recoveries for the other inorganic anions in that fraction. The indicated location of fraction 1 thus remains the best possible compromise for the determination of phosphate simultaneously with other anions under the conditions of

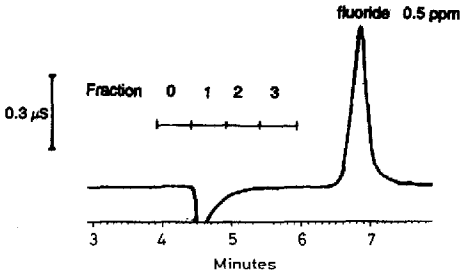


Fig. 5. Ion-exclusion chromatogram of six inorganic anions. The scale indicates the intervals during which the four fractions (0–3, see Fig. 6) were collected. Conditions: columns, two Waters Ion Exclusion (15 × 0.78 cm I.D.) in series; eluent, 1 mM octanesulfonic acid; flow-rate, 1.2 ml/min; sample, 100 μl of 0.5 ppm fluoride, 2 ppm chloride, 4 ppm bromide, 4 ppm nitrate, 6 ppm phosphate and 4 ppm sulfate; detection, Waters M430 conductivity detector.

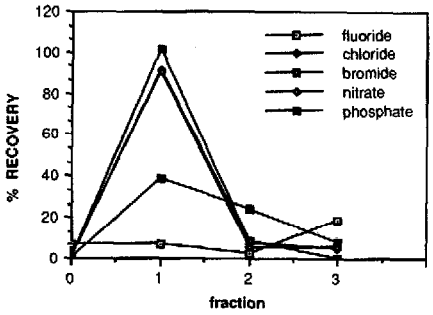


Fig. 6. Recoveries of selected inorganic anions after their transfer from the ion-exclusion to the anion-exchange column. Fractions were taken at intervals indicated in Fig. 5. Note: the distribution curves for chloride and nitrate are overlapped.

coupled dual column system. Since the sulfate was not one of the original components of the mixture injected onto the ion-exclusion column, the corresponding peak in anion-exchange separation in Fig. 7 indicates that traces of sulfate are present in the ion-exclusion eluent and transferred along with the anions from the injected sample. Such contamination by sulfate makes of course any accurate determination of that anion impossible on a coupled system. In the subsequent experiments we could prevent such sulfate contamination by using a higher purity sodium octanesulfonate obtained from a different source (Millipore Corp.). It should be noted that the percentage recoveries for chloride and for nitrate in Fig. 6 are somewhat higher than those listed for the same two anions by direct injection in Table III. These variations of recovery rates are explainable by the fact that the two sets of recovery results were obtained by two different operators on two non-identical coupled systems assembled from the scratch. In both cases the delay volume as represented by the length of the tubing connecting the ion-exclusion and the anion-exchange system were considered to be negligible.

Having thus determined the most suitable section of the ion-exclusion eluate for the transfer to the anion-exchange column we have reinjected the mixture from Fig. 4. The chromatogram in Fig. 8 documenting the resolving power of a coupled system (compare Figs. 4 and 8) was obtained with the help of the fully automated transfer procedure given in Table I and illustrated in Figs. 1 and 2.

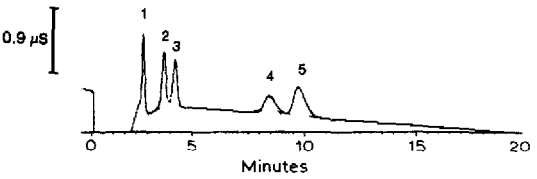


Fig. 7. Anion-exchange separation of fraction 1 from the ion-exclusion chromatogram in Fig. 5. Conditions: flow-rate, 1.2 ml/min. The 3 m*M* sodium octanesulfonate eluent was adjusted to pH = 6.0 using a 1 mg/l LiOH solution. Other conditions as in Fig. 4. Anions: 1 = chloride (2 ppm); 2 = bromide (4 ppm); 3 = nitrate (4 ppm); 4 = phosphate (6 ppm); 5 = sulfate.

TABLE III

RECOVERIES AT ppm AND ppb LEVELS

For acceptable recoveries of weak acids the pH of the preconcentrated samples has to be sufficiently high to ensure a full dissociation of analytes.

Anion	*Concentration (ppm)*	*Injection/preconcentration volume (ml)*	*Recovery (%)*
Chloride	2	0.1	74.1
Nitrate	4	0.1	80.3
Fluoride	0.0033	35	84.4
Formate	0.0067	35	91.2
Acetate	0.0167	35	95.4
Propionate	0.0333	35	87.1
Chloride	0.0067	35	59.7
Nitrate	0.0133	35	60.2

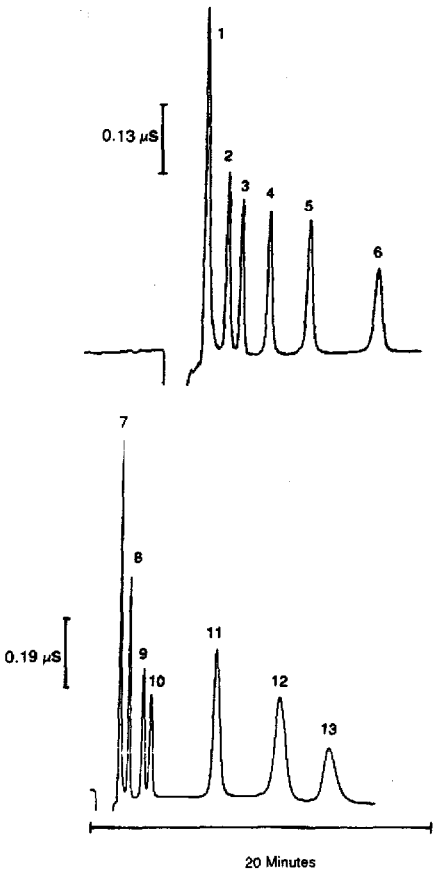


Fig. 8. Simultaneous separation of weakly and strongly acidic anions on a coupled system. Conditions: flow-rate, 1 ml/min for both separation systems; sample, 100 µl of a mixture of strong and weak acid anions. Other conditions were identical with those in Fig. 4 (anion exchange) and in Fig. 5 (ion exclusion). Peak identification and concentrations as in Fig. 4.

Sample preconcentration for the coupled ion-exclusion and anion-exchange separations

Simultaneous preconcentration of weakly and strongly acidic anions is a problem requiring some consideration. For optimum recoveries of weakly ionized anions on anion-exchange concentrator columns one has to make sure that such anions do not have to compete for ion-exchange sites with either more strongly attracted anions from the same sample or with a much greater mass of other anions of comparable strength. Under practical conditions one attempts to fulfill these requirements by providing a sufficiently high anion-exchange capacity on the concentrator and by conditioning the concentrator precolumn with a solution of the lowest possible eluting strength. In the coupled system under discussion 1 m*M* octanesulfonic acid coming from pump 1 is the weaker anion-exchange eluent of the two employed mobile phases. For this reason the automatic sequence depicted in Fig. 3 employs an initial step during which a controlled volume of the ion-exclusion eluent is pumped through the concentrator to condition it for the next sample enrichment (see step 1 in Fig. 3). Duration of step 1 and of all the other steps of the automatic trace enrichment and column coupling procedure is given in Table II. The actual loading of the anions from the sample onto the concentrator is carried out during step 2. In step 3 the preconcentrated anions are eluted from the concentrator and onto the ion-exclusion column by a 0.5-ml segment of the anion-exchange eluent. This is followed by an equal volume of the ion-exclusion eluent from pump 1 (step 4). During step 4 the remaining interstitially held volume of pure water stemming from the sample is replaced by the ion-exclusion eluent. The concentrator column is taken out of the eluent stream in step 5. Fraction one (see Fig. 5) of the ion-exclusion separation is being transferred to the anion-exchange column during step 6. Both, the ion-exclusion and anion-exchange separation run simultaneously and are completed within step 7. Recoveries of several anions with and without the preconcentration procedure just described are given in Table III. The percentage values for chloride and nitrate at relatively high concentrations (2 and 4 ppm) were obtained by comparing peak areas generated using the procedure described in Table I with those measured after a direct injection on the single-column anion-exchange system. These values reflect the efficiency of transfer of strong anions from the ion-exclusion to the anion-exchange system. The remaining data in Table III were collected at concentration levels requiring sample preconcentration. In the case of weak acids (fluoride through propionate) the listed values relate only to the performance of the preconcentration procedure (step 2, Table II) (*i.e.*, at 100% preconcentration efficiency 35 ml of 3.3 ppb fluoride should generate the same peak area as 100 μl of 1.155 ppm of the same anion, etc.). The values of recoveries for sub-ppm levels of chloride and nitrate represent the combined efficiencies of both the sample preconcentration and transfer. With the known recoveries for the fraction transfer determined at ppm levels (chloride 74.1% and nitrate 80%) and the sub-ppm values listed in Table III, the preconcentration efficiencies for chloride and nitrate can now be calculated as 80.5% and 75% respectively. As can be seen in the next section of this article, the relatively low recoveries given in Table III for chloride and nitrate, which result from the two steps just discussed, remain without any negative influence on the reproducibility of the method. A chromatogram showing simultaneous separation of ppb levels of carboxylic acids in a mixture with inorganic anions is presented in Fig. 9.

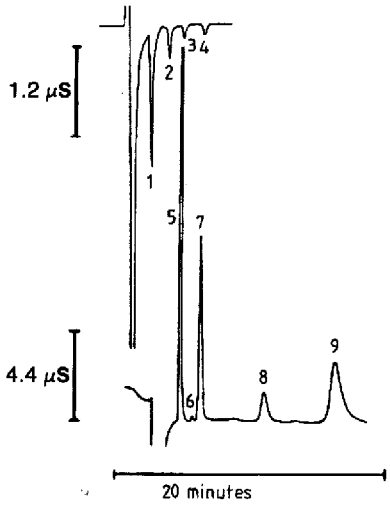


Fig. 9. Chromatogram of ppb concentrations of carboxylic acids and inorganic anions. Conditions: anion-exchange eluent, 2.1 m*M* sodium octanesulfonate; sample, 33 ml of the low-ppb mixture of anions were preconcentrated on a precolumn (CON, Fig. 1). All other conditions were as given in Fig. 8. It should be noted that because of the delayed start of data acquisition for the upper chromatogram (ion exclusion) 2.8 min should be added to the retention times for peaks 1–4. Anions: 1 = fluoride (5 ppb); 2 = formate (5 ppb); 3 = acetate (10 ppb); 4 = propionate (25 ppb); 5 = chloride (25 ppb); 6 = bromide; 7 = nitrate (25 ppb); 8 = iodide (25 ppb); 9 = sulfate (25 ppb).

Reproducibility of separations on the coupled system

Precision of the results on the investigated coupled column system was evaluated at two different concentration levels. In the first series of experiments three repetitive injections were made at five different concentrations not requiring any sample preconcentration (first concentration level: 1–45 ppm, see Table IV). The main purpose of these measurements was to evaluate the reproducibility of the transfer of strongly acidic anions from the dead volume zone of the ion-exclusion column to the anion-exchange separation system. The reproducibility of retention times for each of the peaks of the selected anion standards was calculated from the total of fifteen injections. In all instances the values of the relative standard deviations (R.S.D.) of retention times were found to be less than 0.9%. The relative standard deviations of peak areas were estimated from three analyses performed at each of the five concentrations and are presented in Table IV. The reproducibility of the chloride results was found to be acceptable in the entire investigated range from 1 to 45 ppm. The precision of the results for nitrate and for iodide deteriorated below 15 and 35 ppm, respectively. Given such a kind of concentration dependency of the standard deviations, the increased imprecision for nitrate and for iodide was attributed to the relatively high values of detection limits under the chosen experimental conditions. UV detection is known to provide a better sensitivity for nitrate[11] and amperometry has been shown to enable a more sensitive detection for iodide[12] than the conductivity detection utilized in our work on the coupled systems. Overall, the data in Table IV give an indication that the analysis of strongly acidic anions can be achieved with an acceptable reproducibility with the investigated configuration of the coupled system.

TABLE IV

REPRODUCIBILITY OF PEAK AREAS (% R.S.D.) AFTER THE TRANSFER FROM ION EXCLUSION TO ANION EXCHANGE AT FIVE DIFFERENT CONCENTRATIONS

Concentration 1: 1 ppm chloride, 1 ppm nitrate and 5 ppm iodide; concentration 2: 15 ppm all three anions; concentration 3: 25 ppm all three anions; concentration 4: 35 ppm all three anions; concentration 5: 45 ppm all three anions.

Anion	*Concentration*				
	1	*2*	*3*	*4*	*5*
Chloride	0.8	0.4	0.3	0.4	0.2
Nitrate	3.1	0.2	0.4	0.5	0.1
Iodide	10.5	24.0	9.8	1.2	0.9

Additional evidence is provided by the data in Table V (second concentration level 0.5–45 ppb) generated using the automatic preconcentration and fraction transfer outlined in Table II and illustrated in Fig. 3 (steps 1–7). As in Table IV each value in Table V represents an estimate of the relative standard deviations of peak areas based on three independent measurements. Precision of the results was found to be satisfactory with the exception of that for the peak areas of iodide. As in the previous case it was concluded that the relative imprecision of the results for this anion was caused by the relatively lower sensitivity of conductometric detection. The reproducibility evaluation of retention times was based on twelve data points for each of the anions in Table V. The precision of the retention times at the second concentration level was found to be comparable to that determined at the first concentration level. All corresponding relative standard deviations were equal to or lower than 0.9.

TABLE V

REPRODUCIBILITY OF PEAK AREAS (%R.S.D.) AT FOUR DIFFERENT ppb CONCENTRATIONS (PRECONCENTRATION AND TRANSFER FROM ION EXCLUSION TO ANION EXCHANGE)

Concentration 1: fluoride 0.5 ppb, all other anions at 15 ppb; concentration 2: fluoride 1.0 ppb, all other anions at 25 ppb; concentration 3: fluoride 5.0 ppb, all other anions at 35 ppb; concentration 4: fluoride 10.0 ppb, all other anions at 45 ppb.

Anion	*Concentration*			
	1	*2*	*3*	*4*
Fluoride	6.5	2.2	0.6	1.2
Acetate	2.7	4.2	3.8	6.2
Propionate	13.2	2.6	3.5	1.0
Chloride	3.3	0.6	1.1	1.0
Nitrate	0.9	0.8	1.6	0.9
Iodide	22.0	6.7	12.0	10.0

Extreme sample matrices

At concentration levels not requiring preconcentration the discussed method of column coupling offers considerable advantages in dealing with various difficult matrices without the need for an extensive sample preparation. As has been shown[10] ppm levels of anions are separated without interferences after an injection of samples containing elevated concentrations of boric acid. In a similar manner coupled systems represent a convenient approach to the determination of trace anions in concentrated solutions of for example sodium hydroxide or sodium carbonate[13].

In alkaline solutions the hydroxide molarity is usually two or more orders of magnitude greater than that of the analyte anions present at low-ppb concentrations. During the necessary preconcentration step hydroxide would thus elute most of the other anions from the concentrator column, causing low or near zero recoveries not only for the carboxylic acids but for the most inorganic anions as well. However, as we have found, such interference with the trace enrichment step can be prevented by connecting a column containing a cation-exchange resin in its hydrogen form between the trace enrichment pump and the concentrator (TEP and CON in Fig. 1). The required ion-exchange capacity of the cation-exchange resin can be calculated from the known pH value of the water samples. As long as there are protons available at the cation-exchange sites, alkaline cations are continuously removed from the sample stream and the excess of hydroxide anions disappears into the undissociated water molecules as determined by the ionic product of water. A typical chromatogram obtained from an alkaline water sample using the procedure just described is presented in Fig. 10.

Elevated levels of boric acid usually do not cause any decreases of recoveries during the preconcentration step. As determined by its acidic dissociation constant, boric acid does not compete for the anion-exchange sites below pH 9. On the other hand boric acid, employed as a neutron absorber in nuclear power generating stations,

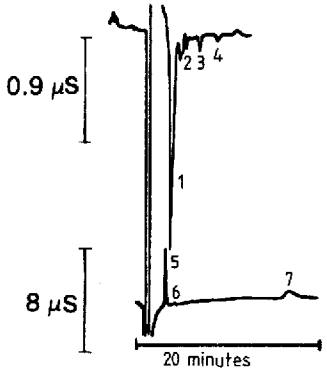


Fig. 10. Water sample from a pressurized water reactor steam generator at pH 9.5. During the preconcentration 33 ml of the sample were pretreated by contact with a strong cation exchanger in the hydrogen form. The cation-exchange resin was packed in a small precolumn connected to the sample line between the sample container and the preconcentrator cartridge, see text. Conditions: cation-exchange precolumn, Waters IC PAK Cation Guard (5.00 × 0.46 cm I.D.); anion-exchange eluent, 1.8 m*M* sodium octanesulfonate. Remaining conditions were as in Fig. 8. Anions: 1 = fluoride (5.5 ppb); 2 = formate (3.0 ppb); 3 = acetate (25.0 ppb); 4 = propionate (20.0 ppb); 5 = chloride (14 ppb); 6 = nitrate (1 ppb); 7 = sulfate (5 ppb).

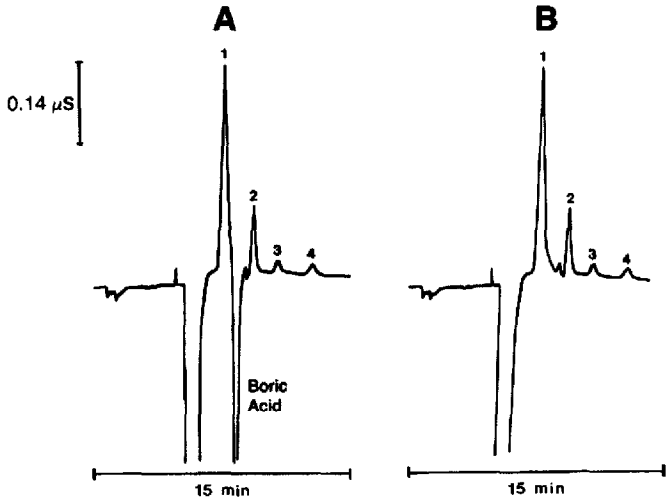
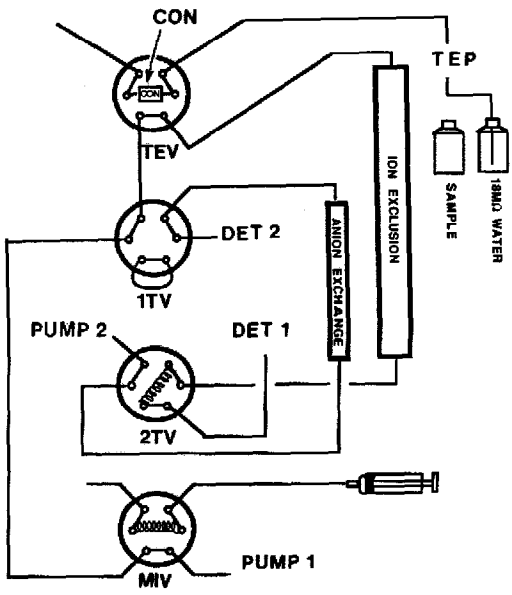


Fig. 11. Synthetic sample from a primary side of a pressurized water reactor prepared by an addition of 2000 ppm boron (as boric acid) to an aqueous solution containing 1 ppb fluoride (1), 2 ppb formate (2), 5 ppb acetate (3) and 10 ppb propionate (4). (A) Ion-exclusion separation using conditions from Fig. 4. A 33-ml volume of the sample was preconcentrated using the procedure outlined in Table II and in Fig. 2. (B) Ion-exclusion separation using water rinsing step for the precolumn. Further details are given in Fig. 12 and in the text.

frequently exceeds the concentrations of other inorganic and organic species in water by a factor of 10^5 and more. Without any additional precaution a small segment of a highly concentrated boric acid solution remains inside the concentrator even after the flow of the sample had been stopped. Under normal conditions (for example in Table II) the preconcentration is immediately followed by an elution step during which the retained anions are transferred to the chromatographic column. In the case of excessive boric acid concentrations the resulting ion-exclusion chromatograms then have the appearance of the one shown in Fig. 11A. Boric acid contained in the interstitial volume of the concentrator resin transfers to the ion-exclusion column along with the anionic species, and since it is also retained, causes a prominent negative conductivity peak disturbing the quantitation of fluoride and formate. Fig. 11B shows an improved separation achieved by a modification of the trace enrichment and fraction transfer procedure. During an additional step inserted between steps 2 and 3 in Fig. 3, the concentrator column is rinsed with approximately 3.5 ml of deionized water. In this fashion the interstitially held boric acid is completely removed while the recoveries of anionic analytes during the subsequent steps remains identical with those in Table III. Instrumental configuration during such rinsing is given in Fig. 12.

CONCLUSIONS

Using the methods described in this report it is possible to overcome the limitations of anion-exchange separations. With the help of eqn. 1 the total number of "resolvable peaks" on the anion-exchange column is calculated as $n_r = 3$ in an obvious agreement with the experiment represented by the chromatogram in Fig. 4. Estimating



STEP 3

Fig. 12. Coupled system configuration during the rinsing step. Removal of excess boric acid from the concentrator column. After completion of step 2 in Table II the automatic program is interrupted. The trace enrichment pump is stopped and the sample line is immersed in a precleaned container filled with ultra high purity water. TEP is turned on again and *ca.* 6 ml of clean water containing no more than low-ppt concentrations of anions of interest are pumped through the concentrator (CON). After the successful removal of boric acid from the concentrator column the automated program continues with step 3.

the available range of retention volumes on the ion-exclusion system as $V_R/V_0 = 14/4$ and the separation efficiency $N = 5000$ as well as taking into account eqn. 2[5]

$$n_r = 0.18(n_{c1} + n_{c2}) \quad (2)$$

where $n_{c1} = 16$ represents the peak capacity of the anion-exchange separation and $n_{c2} = 23$ the peak capacity of the ion-exclusion separation. The total number of resolvable peaks is calculated as $n_r = 7$. According to the definition of n_r and in agreement with the experimental data, the coupled ion-exclusion and anion-exchange system is shown to provide sufficient resolving power to be able to separate many of the known mixtures of early eluting anions and carboxylic acids. The simultaneous analysis of weak and strong anions using the described instrumental procedure allows a fast determination of weakly and strongly dissociated anions in a large variety of water samples. The analysis is largely independent of the typical sample matrices encountered in the power generating and semiconductor industries.

REFERENCES

1 *Guidelines for Pure Water*, Technical Document I-85, Semiconductor Equipment and Materials Institute, Mt. View, CA, 1985.
2 J. P. Denoncourt and Y. Egozy, *Ultrapure Water*, 3 (1986) 40.

3 M. M. Plechaty, *LC · GC, Mag. Liq. Gas Chromatogr.*, 2 (1984) 684.
4 G. D. Burns, R. C. Nolan, J. E. Crutchfield and T. O. Passel, *Proceedings 47th International Water Conference, Pittsburgh, October 27–29, 1986*, Engineer's Society of Western Pennsylvania, Pittsburgh, PA, Paper No. 12, pp. 105–119.
5 J. C. Giddings, *Anal. Chem.*, 56 (1984) 1259 A.
6 J. C. Giddings, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 319.
7 J. C. Giddings, in H. J. Cortes (Editor), *Multidimensional Chromatography: Techniques and Applications*, Marcel Dekker, New York, in press.
8 W. R. Jones, P. Jandik and A. L. Heckenberg, *Anal. Chem.*, 60 (1988) 1977.
9 R. D. Rocklin, C. A. Pohl and J. A. Schibler, *J. Chromatogr.*, 411 (1987) 107.
10 W. R. Jones, A. L. Heckenberg and P. Jandik, *J. Chromatogr.*, 366 (1986) 225.
11 P. R. Haddad and P. Jandik, in J. Tarter (Editor), *Ion Chromatography*, Marcel Dekker, New York, 1986, p. 128.
12 P. Jandik, D. Cox and D. Wong, *Am. Lab. (Fairfield, Conn.)*, 18 (1986) 114.
13 W. R. Jones, W. J. Wildman, A. L. Jagoe, A. L. Heckenberg and P. Jandik, presented at the *Pittsburgh Conference and Exposition, Atlantic City, NJ, March 10–14, 1986*, Abstract No. 074.