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DETECTION OF TRACE ORGANIC IMPURITIES IN BINARY SOLVENT SYSTEMS: A SOLVENT PURITY TEST

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SUMMARY

A convenient solvent purity test that distinguishes between trace organic impurities present in either organic solvents miscible with water or in water is described. It utilizes the reversed-phase liquid chromatographic trace-enrichment technique by which solvent impurities are concentrated onto the inlet end of a reversed-phase column. The complete test procedure consists of a specific series of gradient elution runs conducted under standardized conditions in both the forward and reverse directions after first subjecting different volumes of each pure solvent to trace enrichment. The resulting set of gradient elution profiles produces a wealth of chromatographic information, the interpretation of which enables the origin of impurities present in a binary solvent system to be determined. Tests show that acetonitrile is relatively pure but that trace impurities present in methanol or tetrahydrofuran can exceed and mask those present in water. The efficacies of some treatments designed to remove trace organic impurities from water are evaluated using the solvent purity test.

INTRODUCTION

Various impurities normally present in solvents used for high-performance liquid chromatographic (HPLC) analysis can cause serious problems. Their adverse effect on baseline dirft, signal-to-noise ratio, and sensitivity in trace analysis when using isocratic elution, and on the occurrence of large baseline fluctuations and spurious interfering peaks when using gradient elution, have been discussed[1,2]. Undected solvent impurities can accumulate by adsorption on the inlet end of a costly HPLC column to shorten its useful life. Artful and time-consuming regeneration procedures have been recommended to solve this problem but are of limited effectiveness. The use of a guard column to protect the analytical column is strongly encouraged[1–3]. However, the longevity of a guard column will be dependent on the nature and concentration of impurities present in mobile phase solvents.

Because of these problems, highly purified solvents are needed to perform sensitive and accurate HPLC analyses. It is usually trace organic rather than inorganic

impurities in solvents that cause problems. However, the available tests which detect trace organic impurities in organic solvents are inadequate; traditional measurements of solvent UV cutoff point, residue after ignition, refractive index, or boiling point range are not nearly as sensitive as needed. Commercial suppliers of solvents for HPLC have begun to recognize the problem[2]. It is quite apparent that a convenient test that evaluates organic solvent purity with respect to the presence of trace organics for various trace analytical applications including HPLC is badly needed.

The solvent purity test reported here is fast and simple. It was adapted from the single blank run procedure recommended for the characterization of water related artifacts that frequently occur during reversed-phase liquid chromatographic (RPLC) analysis utilizing gradient elution[1,4,5]. It goes beyond the single blank run procedure for water since it recognizes that trace organic impurities can and do originate in the organic solvents used for RPLC analysis and distinguishes them from those present in water. It consists of a series of linked gradient elution runs conducted in both the forward and reverse directions under standardized conditions. It can be applied to any organic solvent miscible with water in all proportions and permits assignment of the origin of trace impurities present in binary aqueous–organic solvent mixtures. It should be possible to extend this procedure to other modes of LC and to non-polar organic solvents.

EXPERIMENTAL*

Apparatus

A liquid chromatograph, Model ALC 204 (Waters Assoc., Milford, Mass., U.S.A.) consisting of Series 6000 and Series 6000A solvent delivery systems controlled by a Model 660 solvent programmer, a Model U6K injector, and a dual-channle Model 440 absorbance detector operated at 254 and 280 nm was used throughout this study. Two columns (Waters Assoc.) were utilized in this work. For gradient elution RPLC, a 300 × 3.9 mm μBondapak C_{18} column was operated at room temperature. In one experiment, a 610 × 2 mm C_{18}/Porasil B (37–50 μm) column was inserted as a finisher or guard column between the outlet of the Series 6000 pump, which was used to deliver water, and the mixing valve of the Series 6000A pump. Chromatograms were recorded on a Honeywell-Electronic 196 dual-channel recorder at a chart speed of 0.5 in./min.

Chromatographic-grade water was obtained from a Milli-Q-Reagent-Grade water system[4,5] (Millipore, Bedford, Mass., U.S.A.). After installation of cartridges or any change in cartridge order, at least 30 l was passed through the system before water was collected for use in RPLC gradient elution work.

Reagents

Organic solvents, either distilled-in-glass or UV grade, as available, were purchased from Burdick & Jackson Labs. (Muskegon, Mich., U.S.A.). Solvents were

* Use of trade names is for identification purposes only and does not constitute endorsement by the Environmental Protection Agency.

degassed by vacuum filtration through a membrane filter or by overnight magnetic stirring.

Solvent purity test procedure

The standard operating parameters selected for RPLC gradient elution analysis utilized a mobile phase flow-rate of 4.0 ml/min and a 10%/min linear gradient ("curve 6" on the Model 660 solvent programmer) from 0 to 100% in either direction. Detector sensitivity was selected so that baseline drift from beginning to end of a gradient run was <25% of full scale. Thus, the actual attenuation used depended on the observed difference in absorbance between the pure aqueous and the pure organic modifier solvent being evaluated.

A complete mobile phase solvent purity test for a binary solvent mixture consisted of four or five gradient elution profiles linked together. To obtain the first, the impurities from 40 ml of water (solvent A) were concentrated onto the column under isocratic conditions (10 min at 4.0 ml/min) before a gradient was run from 0 to 100% organic modifier solvent (solvent B), as done in a simple blank run[1,4,5]. Then, without changing any conditions, a minimum of 10 ml of organic solvent was pumped through the column before a reverse gradient was executed from 0 to 100% solvent A to produce the second gradient elution profile. Next, depending on the peak heights obtained in the first gradient elution profile, the volume of water subjected to trace enrichment was either increased or decreased by a factor of 2 to 4 by altering the duration of the isocratic pumping period and a third gradient elution profile was obtained. Finally, after 40 ml or more of organic solvent had flushed the column, the cumulative volume or organic solvent passed through the column during the process of returning the gradient to initial conditions (100% solvent A) was decreased by lowering the flow-rate from 4.0 to 1.0 ml/min during the reverse gradient. Just as the mobile phase composition reached 100% water, the system was reset to standard operating parameters (4.0 ml/min flow-rate, 10%/min linear gradient). Before a significant volume of water could pass through the column under isocratic conditions, a fourth gradient elution profile was obtained. This usually completed the series of gradient elution profiles. However, if the second gradient elution profile exhibited discrete peaks, then the volume of organic solvent pumped over the column under isocratic conditions (100% solvent B) was altered by a factor of 2 to 4 before a reverse gradient was executed to give a fifth gradient elution profile.

The trends within and the differences between the 4 or 5 gradient elution profiles thus obtained were interpreted to reveal the source and relative levels of the trace impurities present in the individual solvents of binary mixtures.

RESULTS AND DISCUSSION

The principes and practice of macro-scale trace enrichment as a step in the analysis of organic contaminants in water samples are well documented[6–10]. The advent of HPLC, with its bonded stationary phase columns and gradient elution solvent programming techniques, has enabled the trace enrichment technique to be further developed into a rapid, micro-scale method based on RPLC for the analysis of a wide variety of trace organics in water[4,5,11]. The RPLC method involves concentration of organic impurities from aqueous samples by sorption onto the inlet end

of a reversed-phase column. Subsequent gradient elution separates the sorbed organic solutes for direct detection by UV or other detectors, or for collection and subsequent detection by other means. Because solvent water, as distinguished from sample water, is passed through the column in large volume as the mobile phase during the purge and gradient elution steps of the RPLC trace enrichment method, it must be particularly free of trace organic impurities itself.

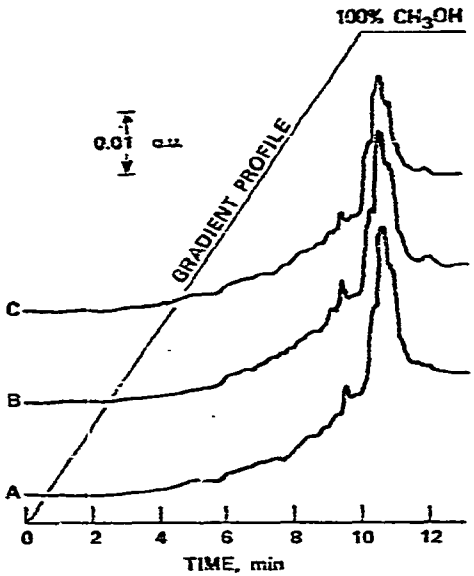

Fig. 1. RPLC gradient elution profiles of: (A) 0 ml, (B) 160 ml, and (C) 40 ml of Milli-Q treated water monitored at 254 nm, 0.1 a.u.f.s. Mobile phase composition was programmed from 0 to 100% methanol at 10% /min. For (C), only 5 rather than the usual 20 ml of methanol was used in returning the gradient from 100% methanol to initial conditions.

The RPLC trace enrichment-gradient elution method[4,5,11] was used to evaluate the quality of water obtained from a newly installed Milli-Q system for water purification. Fig. 1 shows some gradient elution profiles resulting from blank runs made under the standard operating conditions described above. The mobile phase consisted of Milli-Q treated water–methanol. The profiles reveal that surprisingly large amounts of late eluting and therefore nonpolar contaminants are present in the binary mobile phase. When the volume of Milli-Q system water subjected to trace enrichment was increased from 0 to 160 ml (Fig. 1A and B), peaks in the gradient elution profile did not increase in size as expected[4,5]. In addition to the Milli-Q system water, 40 ml samples from several different distilled and deionized water sources were subjected to RPLC trace enrichment–gradient elution analysis using the same Milli-Q water–methanol mobile phase. While these samples were expected to contain different amounts of trace organic impurities and therefore produce different profiles, they produced identical profiles that were indistinguishable from those produced by the Milli-Q system water samples (Fig. 1A and B).

These results suggested that although different amounts of trace organic contaminants were undoubtedly present in the rather pure water samples being tested, they were being masked by impurities present in the organic modifier solvent, methanol. In order to confirm this conclusion, the complete mobile phase solvent purity test procedure described above was developed. The required sequence of four gradient elution profiles for the water–methanol binary mobile phase solvent is given by Figs. 1A, 2A, 1B and 1C, respectively. Although not shown, when profiles were monitored at 280 nm, the peaks and baseline shifts observed were nearly identical in pattern but weaker in intensity than those monitored at 254 nm.

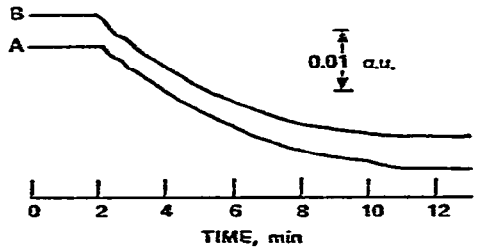

Fig. 2. RPLC reverse gradient elution profiles of: (A) 20 ml and (B) 80 ml of methanol monitored at 254 nm, 0.1 a.u.f.s. Mobile phase was programmed in the reverse direction from 100 to 0% methanol at 10%/min.

The 14% decrease in peak height for the profile of Fig. 1C relative to the identical peak heights for Fig. 1A and B demonstrates conclusively that the impurities observed in the gradient elution profiles come from the methanol rather than the water used in the mobile phase. Apparently, during the reverse gradient (Fig. 2), as the mobile phase increases in water content and becomes a weaker elution solvent for RPLC, any non-polar organic impurities present in the mobile phase are sorbed onto the inlet end of the column, regardless of their origin. The same is true during the initial stages of gradient elution as small amounts of methanol are blended with large amounts of water. In this sense, the mechanism of the trace enrichment process is the exact opposite of that governing gradient elution; solutes are sorbed onto or desorbed from a reversed-phase bonded surface such as a C_{18} column packing depending on their polarity, the elution strenght of the mobile phase, and the direction of the gradient.

For example, during the early stages of gradient elution in Fig. 1 (roughly 0–50% methanol), the mobile phase is weak. Impurities present in either the organic solvent or water are introduced constantly but are sorbed onto the inlet end of the column and thereby prevented from reaching the detector. Non-polar impurities are retained until the mobile phase becomes stronger (50–100% methanol). As impurities in the progressively stronger mobile phase begin to pass through the column and reach the detector, a positive baseline drift is produced. This levels off after the mobile phase composition is 100% methanol and impurities are no longer retained by the column but reach the detector at a constant concentration level. Superimposed on the drifting baseline are peaks that correspond to impurities that were sorbed from the binary solvent mobile phase onto the column inlet either: (a) during the trace enrichment step (or injection) prior to the start of a run, (b) during the early

stages of the gradient elution run, or (c) during the latter stages of the reverse gradient used routinely to regenerate the initial run conditions. The complex nature of the resulting chromatogram is the result of the dynamic, non-equilibrium process associated with gradient elution.

In Fig. 2, no impurities are removed from either the 100% methanol passed through the column during isocratic loading nor from the programmed mobile phase until it begins to be diluted in elution strength by addition of water and becomes weak enough for non-polar impurities to begin to be removed from it by trace enrichment. As progressively fewer impurities reach the detector, a negative baseline drift occurs. During the latter stages of the reverse gradient (50–0% methanol), all impurities are sorbed efficientiy and the baseline levels off. No peaks are superimposed on the baseline because mobile phase elution strength was decreased during the reverse gradient.

While it might seem surprising that trace enrichment of solvent impurities could occur from mobile phase containing as much as 80% methanol, Otsuki[11] has shown that butyl and higher phthalate esters are retained very efficiently for over 60 column volumes by a reversed-phase column with isocratic mobile phase strengths as high as 50 and 60% in methanol. Accordingly, solutes less polar than phthalate esters, such as high-molecular-weight polycyclic aromatic hydrocarbons, chlorocarbons, polychlorinated biphenyls, open-chain hydrocarbons, etc., should be subject to trace enrichment from mobile phase solvent systems of even greater eluting strength.

The use of acetonitrile instead of methanol as the organic modifier solvent for gradient elution provided additional evidence that the solvent impurities revealed in Fig. 1 originated in methanol rather than water. As shown in Fig. 3, the overall baseline

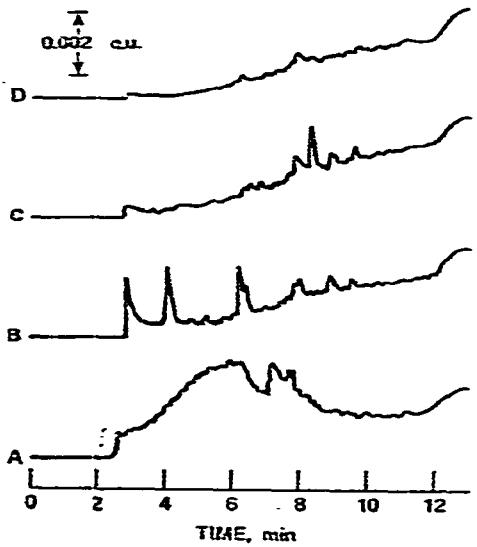

Fig. 3. RPLC gradient elution profiles of: (A) 40 ml of house-deionized water; (B) 40 ml of Milli-Q system water, manufacturer's recommended cartridge configutation; (C) 40 ml of Milli-Q system water with carbon cartridge at end of train; (D) 0 ml water as in (C) monitored at 254 nm, 0.02 a.u.f.s. Mobile phase composition was programmed from 0 to 100% acetonitrile at 10%/min.

drift observed for a gradient elution profile using water–acetonitrile as the mobile phase is only about 0.003 absorbance unit (a.u.) while the corresponding value using methanol was 0.02 a.u. This suggests that the methanol used contains about 7 times more UV-absorbing equivalents due to trace impurities than does the acetonitrile. Fig. 3A–C shows that water samples representing different degrees of purification do indeed produce different gradient elution profiles when analyzed using Milli-Q water–acetonitrile as the mobile phase. Trace organic impurities present in the water samples are not masked by impurities originating in the organic modifier solvent. Furthermore, Fig. 3C and D reveal that almost all of the impurities observed as peaks orginate in the water of the binary mobile phase solvent system since the peak heights are directly proportional to the amount of water subjected to trace enrichment before the run is started.

In contrast to methanol, the reverse gradient elution profile for acetonitrile gave rise to a group of solvent impurity peaks. These must originate in the acetonitrile since their peak heights are directly proportional to the amount of acetonitrile pumped onto the column (Fig. 4). Different batches of acetonitrile produced the same pattern of peaks which varied in relative intensity, however. The nature of the impurities is not clear except that their absorbance at 280 nm was twice that at 254 nm. Assuming that these impurities are organic solutes, their retention behavior is anomolous; organic solutes are not normally retained by a reversed-phase column when the mobile phase consists of 100% organic solvent and then eluted by water. Accordingly, the observed impurities may correspond to very polar or ionogenic solutes present in pure acetonitrile that are strongly sorbed to or undergo ion exchange with unreacted silanol sites of the silica stationary support.

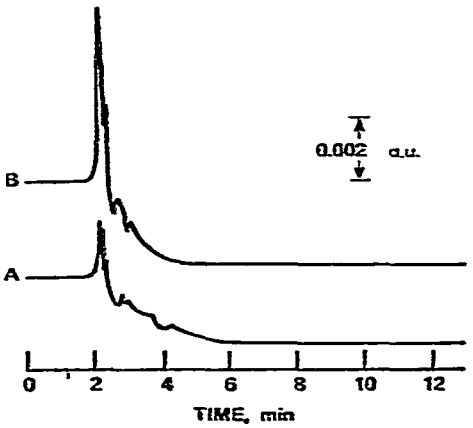

Fig. 4. RPLC reverse gradient elution profiles of: (A) 10 ml and (B) 40 ml of acetonitrile monitored at 254 nm, 0.02 a.u.f.s. Mobile phase composition was programmed from 100 to 0% acetonitrile at 10% /min.

The position of the first peaks in Fig. 4 at about 2.1 min may correspond to the time required for the first traces of water in the programmed mobile phase to sweep through the chromatographic system, displace weakly retained solutes, and reach the detector. Elution of a sorbed solute with this initial change in solvent com-

position corresponds to displacement chromatographic analysis[12]. The same effect is observed in Fig. 3 at about 2.5 min and may correspond to the displacement of some weakly sorbed solutes by the first traces of acetonitrile migrating through the system. The slightly larger retention volume observed for displacement using acetonitrile (10 *vs.* 8.4 ml) may be the result of both stronger retention of the sorbed impurities as the gradient elution profile is developed in the normal direction of increasing elution strength and significant solvation of the stationary phase by acetonitrile[13]. The approximately 8.4 ml volume required for the change in solvent composition to reach the detector in Fig. 4 may correspond to the total volume of the chromatographic system that exists between the solvent mixing chamber and the detector. It includes the column void volume (estimated at 1.64 ml) using 100% acetonitrile and all of the extra-column volumes associated with the solvent delivery system. This interpretation is consistent with the observation that the gradient elution profiles in Fig. 3 do not finally level off until about 12.5 min, 2.5 min after the 10 min electronic gradient has been completed. For chromatographic systems having different extra-column volumes associated with solvent mixing, pumping, and transfer tubing, different displacement volumes or volumes required for the initial and final changes in mobile phase composition to reach the detector can be observed. The lag time between the electronic execution and the mechanical achievement of a mobile phase gradient is quite apparent when running the solvent purity test procedure.

While considering this displacement effect, it is interesting to note that the solvent purity test employed here (0 to 100% gradients), makes use of each of the three possible chromatographic development modes[12]. During the isocratic trace enrichment step, which concentrates the sample onto the column, the system is operated in the frontal development (analysis) mode but solute migration is insignificant (solute breakthrough is undesirable). With initiation of the gradient run, the first trace of the modifer solvent sweeps through the chromatographic system, creates non-equilibrium conditions, and causes some weakly sorbed solutes to migrate along with it in the displacement mode. During the rest of the gradient run, solutes migrate through the column by the most common and familiar elution mode of chromatography.

It is not necessary to invoke a refractive index (RI) effect in order to explain the characteristic baseline drift that is observed during gradient elution using a UV detector. Selective sorption-desorption of UV absorbing impurities that are present in mobile phase solvents, as described above for the solvent purity test profiles, accounts for at least a significant part of the observed baseline drift. The differences between the RI values of RPLC solvents alone do not account for this effect; those for pure water, methanol, and acetonitrile at 25° are very close together in magnitude: 1.332, 1.326, and 1.342, respectively. While the net change in RI for a gradient elution run involving water–acetonitrile is larger than that for water–methanol (0.010 *vs.* — 0.006 RI units), the observed magnitude of baseline drift for the solvent pairs (*i.e.*, Δ a.u.) is the opposite. Based on absolute RI values, a water–methanol gradient should produce a baseline drift that is opposite in direction to that predicted for water–acetonitrile. Furthermore, the RI function for mixtures of water–methanol goes through a maximum of 1.343 at 50% methanol in water[14]. If solvent RI was the most important effect in determining the shape of the baseline drift, an approximately symmetrical maximum should be observed, but is not (Figs. 1 and 2). If RI

effects are important, they need to be evaluated after first taking into account changes in the UV absorbance associated with impurities present in the organic solvent(s) used to effect gradient elution.

When acetonitrile was used as the organic modifier in the solvent purity test, the UV absorbing impurities present in water samples of different origin and the efficacy of some treatments designed to remove trace organic impurities from water could be evaluated[5]. Untreated tap water (40 ml) produced an off-scale response with the detector sensitivity set at 0.02 a.u.f.s. The house-deionized water produced a a gradient elution profile that is characterized by a broad absorption envelope of polar and semi-polar impurities (Fig. 3A). Passage of the house-deionized water through a Milli-Q water purification system provided considerable cleanup as most of the broad absorption envelope was removed (Fig. 3B). The remaining peaks in Fig. 3B represent either individual solutes in the feed water that are not removed by the Milli-Q system or solutes leached from the Milli-Q system.

In the normal configuration recommended for the Milli-Q system, water is passed first through a carbon cartridge, then through two ion-exchange cartridges. Reversal of this order by placement of the carbon cartridge at the end of the train had two effects. It resulted in the removal of additional polar and semi-polar trace organic impurities from the feed water (Fig. 3C) and the resistivity of the output water dropped to less than 0.5 MΩ·cm. The solvent purity test is a much better indicator of either organic or aqueous solvent purity with respect to trace organics than is resistivity because resistivity is essentially a measure of ionized inorganic solute concentration. Organic solutes are either non-ionic or, if ionogenic, exhibit low solution mobilities. In either case, even high concentrations of trace organics have little influence on solvent resistivity compared with trace inorganics. The large drop in resistivity of the output water when the cartridge order of the Milli-Q water system was reversed probably stems from leaching of trace inorganic ions from the carbon cartridge but is of little consequence in this application[15]. An improved system designed to remove trace organics but not inorganics from water might utilize a series of cartridges containing different organic scavenging media such as activated carbon, XAD resin, polyurethane, cellulose triacetate, and/or Silicalite. The purity of output water might then be measured using a simple fixed wavelength UV detector or other detectors sensitive to trace organic impurities.

Fig. 3D represents the minimum solvent blank that was obtained using the Milli-Q system with the cartridge reversed (0 ml loaded onto the column). This profile is certainly suitable for the analysis of samples injected into the system after pretreatment and/or preconcentration off-column.

Most of the organic impurities remaining in the water obtained from the Milli-Q system set up with the cartridge order reversed (Fig. 3C) were removed by in-line passage through a column packed with Bondapak C_{18}/Porasil B (Fig. 5A). This column was inserted into the LC system between the pump used to deliver water and the solvent mixing valve in which water and organic solvent were mixed. This combination not only produced the highest quality water for use in RPLC gradient elution but was very convenient. The size and capacity of such a "finisher" column is limited only by the pressure tolerated by the LC system used. For regeneration, the column was removed, connected to the pump delivering acetonitrile and flushed with 25–30 column volumes of solvent. A permanent installation could be

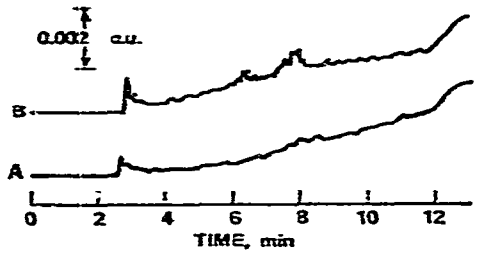

Fig. 5. RPLC gradient elution profiles of 40 ml Milli-Q water samples: (A) using an in-line finisher column of Bondapak C_{18}/Porasil B and (B) feed water pretreated by passage through commercial reversed osmosis and ion exchange systems. Run parameters as in Fig. 3.

made using switching valves. The separation efficiency of the analytical column for injected samples prepared for analysis off-column is not affected because they never come into contact with the "finisher" column. Bondapak C_{18}/Porasil B and Porapak Q have been used to finish the purification of water on a macro-scale, off-line[4] with the possible advantage that column regeneration can be accomplished independently. An in-line "finisher" column cannot be used without switching valves when the sample to be analyzed must be loaded onto the column using the LC pumping system as described in the RPLC trace enrichment technique[1,4,5].

The combination of pretreatment of house-deionized water by passage through a commercial reversed-osmosis system and then through a Milli-Q system assembled in the normal configuration resulted in the gradient elution profile shown in Fig. 5B. Reversed osmosis removed many of the same trace organic impurities that were removed by reversal of the cartridge order of the Milli-Q system (Fig. 3B and C).

The purities of several different water samples obtained by distillation were evaluated. Their gradient elution profiles (Fig. 6) were indicative of organic contamination at levels greater than those found in either the house-deionized water (Fig. 3A) or in water from the modified Milli-Q system (Fig. 3C). Pure water, stored for more than a few days at room temperature, may develop a profile similar to that of Fig. 6B which is indicative of microbial contamination.

In addition to water, the solvent purity test described in this work can be used to evaluate the purity of any organic solvent that is miscible in water. Any detector compatible with gradient elution analysis can be used, but with the UV detector used here, acetonitrile proved to be better suited to trace analysis applications than either methanol or tetrahydrofuran. One sample of tetrahydrofuran evaluated was too contaminated to be useful in gradient elution analysis, even at low detector sensitivity (2.0 a.u.f.s.). It should be possible to extend the solvent purity test procedure to solvents not miscible in water by using the non-aqueous RPLC technique, *e.g.*, hexane–isopropanol or acetonitrile–methylene chloride monitored at 280 nm by UV.

Based on evaluation of the purity of water samples produced by a variety of different treatments, high purity water for use in gradient elution RPLC analysis might be produced most conveniently by a combination of systems as needed. For example, an excellent solvent blank was obtained when house-deionized water, purified by reversed osmosis, was passed through a Milli-Q water purification system

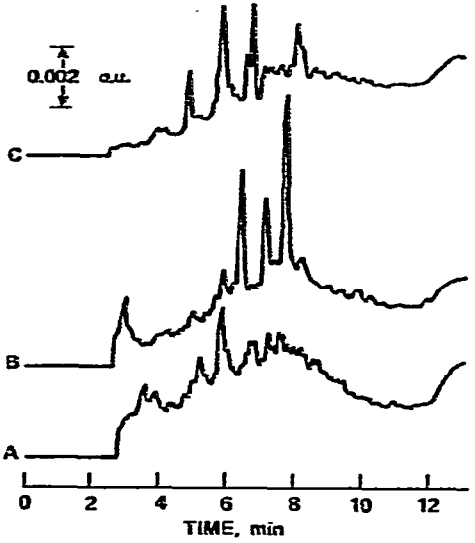

Fig. 6. RPLC gradient elution profiles of water samples; (A) 40 ml of water distilled from sulfuric acid in a Corning still Model AG-2 (tap water feed); (B) 40 ml of water distilled from a Kontes Model WS-2 still (house-deionized water feed); (C) 40 ml of water obtained as in (B) and further distilled from sulfuric acid in an all-glass apparatus. Run parameters as in Fig. 3.

in its normal configuration. Replacement of the last ion exchange cartridge by a carbon cartridge would probably result in even further removal of trace organics[15]. For the most demanding trace analyses, a finisher column can be inserted into the LC pumping system as described.

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