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ANALYSIS OF ppb LEVELS OF ORGANICS IN WATER BY MEANS OF PURGE-AND-TRAP, CAPILLARY GAS CHROMATOGRAPHY AND SELECTIVE DETECTORS

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SUMMARY

The Environmental Protection Agency (EPA) has issued a series of methods (500 and 600 series) for the analysis of organics in drinking water and industrial discharges. Methods 601 and 602 employ packed-column gas chromatography (GC) with electrolytic conductivity (EICD) and photoionization detection (PID), respectively. A purge-and-trap system is used for concentration of volatiles. The EPA is in the process of converting methods 601 and 602 and certain 500-series methods to capillary column analysis. We have also initiated the conversion of a number of these methods, using EICD and PID and have described them in detail in this paper. We have evaluated both 0.32- and 0.53-mm diameter capillary columns, using helium and nitrogen as carrier gases with each detector. We found that with nitrogen optimum results are obtained at a flow-rate of 15 ml/min, and with helium at 6–8 ml/min. As a result of system optimization, including operation of the two detectors in series, and converting from packed to capillary columns, we found that analysis time could be reduced from 80 min (for two methods separately) to *ca.* 30 min. In addition, the elution of more than five components in one peak, observed when the packed column specified in method 601 are used, was eliminated.

INTRODUCTION

In the late 1970s, the United States Environmental Protection Agency (EPA) published methods for industrial discharges which have been designated the 600 series methods¹. EPA method 602 specified the HNU photoionization detector for industrial discharges and method 503.1 for drinking water. Method 601 (chlorinated hydrocarbons) with electrolytic conductivity detection (EICD) is frequently performed together with method 602. Since many of the 600 series methods were for low-molecular-weight hydrocarbons, easily lost by direct injection, a purge and trap technique was developed for analysis of these "purgable pollutants"². This resulted in a series of methods for the analysis of organics in water designated by the EPA as 601–613, 624, 625, 1624 and 1625³.

The 600 series methods were originally developed for analysis on packed columns. With the recent interest in capillary column technology, considerable efforts are underway at the EPA⁴ and at private laboratories⁵⁻⁷ to convert the packed column methods to capillary columns methods. We^{5,6} have already reported on procedures for 0.75 and 0.53 mm I.D. capillary columns. However, an optimization of these methods has not yet been reported.

The purpose of the present paper is to extend our previous work to include 0.32 mm I.D. capillary columns and to study the effects of flow-rate and the nature of the carrier gas on column efficiency. Other objectives are optimization of the detection of volatile chlorinated hydrocarbons by EICD, and of benzene and toluene by PID.

EXPERIMENTAL

The experiments were carried out with HNU (HNU Systems, Newton, MA, U.S.A.) Models 321 or 421 gas chromatographs, equipped with an integral HNU PID (10.2 eV lamp), or a Model 4420 electrolytic conductivity detector (OI Corp., College Station, TX, U.S.A.), and an OI Model 4460 purge-and-trap (sample concentrator). The sample is sparged from an aqueous solution using the carrier gas, concentrated on a solid sorbent, then thermally desorbed into the gas chromatograph where, after separation on the column, the sample is passed first into the photoionization detector, then into the electrolytic conductivity detector. The data were collected on a Nelson Analytical (Cupertino, CA, U.S.A.) personal computer integrator. Prepurified nitrogen or helium was used as the carrier gas for the gas chromatographs and the purge-and-trap. All chemicals were of ACS grade or equivalent. The 601 and 602 standards were obtained from Supelco (State College, PA, U.S.A.). The column packings specified in EPA methods 601 and 602 (packed column methods) were also obtained from Supelco. These column materials were packed in 6 and 8 ft. stainless-steel columns, as prescribed in the Federal Register¹. The 0.32 and 0.53 mm I.D. 624 Halomatic (1.0 and 3.0 μm film thickness, respectively) capillary columns were purchased from Quadrex (New Haven, CT, U.S.A.).

RESULTS AND DISCUSSION

In earlier papers^{5,6} we have discussed the conversion of packed to capillary columns, including the 0.75 mm I.D. Vocal column suggested by the EPA. Using chromatographic conditions similar to the packed column methods, we were able to resolve all 36 components required in methods 601 and 602. Due to the non-destructive nature of PID, the use of a second detector such as the electrolytic conductivity detector, in-series with the photoionization was possible. No problems were encountered, but our recent work on optimization revealed difficulties in eliminating water interference from PID while analyzing the low boiling (b.p. < 35°C) chlorinated hydrocarbons with EICD. This will be discussed in detail below. A major difficulty with this column was fragility since the 0.75 mm I.D. capillary is constructed of borosilicate glass with fused-silica ends. We were able to reduce the analysis time from 50 min for packed columns to 30 min for the 0.75 mm I.D. capillary. In addition, both analyses could be run simultaneously. Later⁶, we found that we could ad-

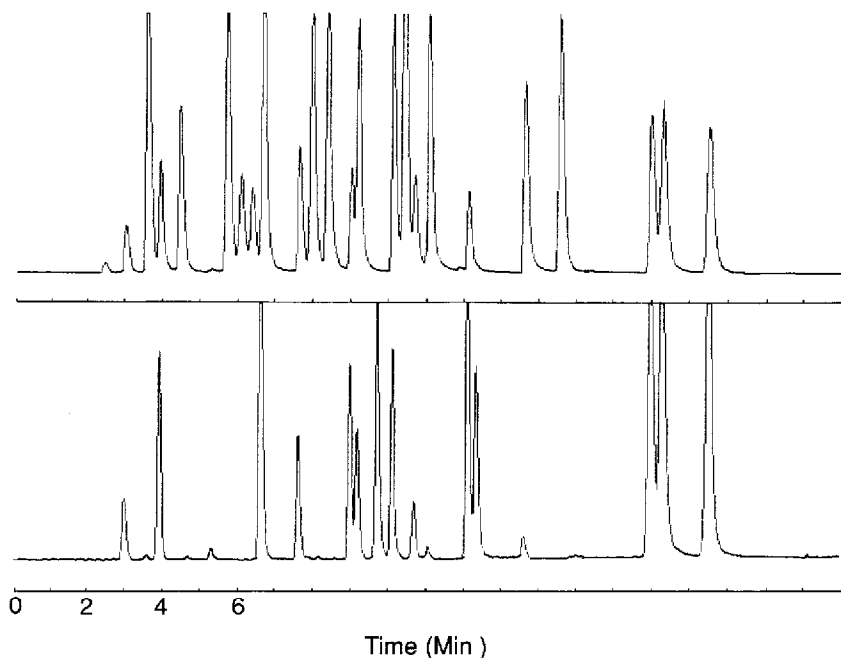


Fig. 1. Typical analysis of EPA 601/602 by capillary gas chromatography with PID and EICD in series. (Top) EICD, (Bottom) PID. Conditions: nitrogen carrier gas 15 ml/min. Initial temperature 35°C for 3 min. then at 8°C/min to 120°C with 15 min hold at 120°C.

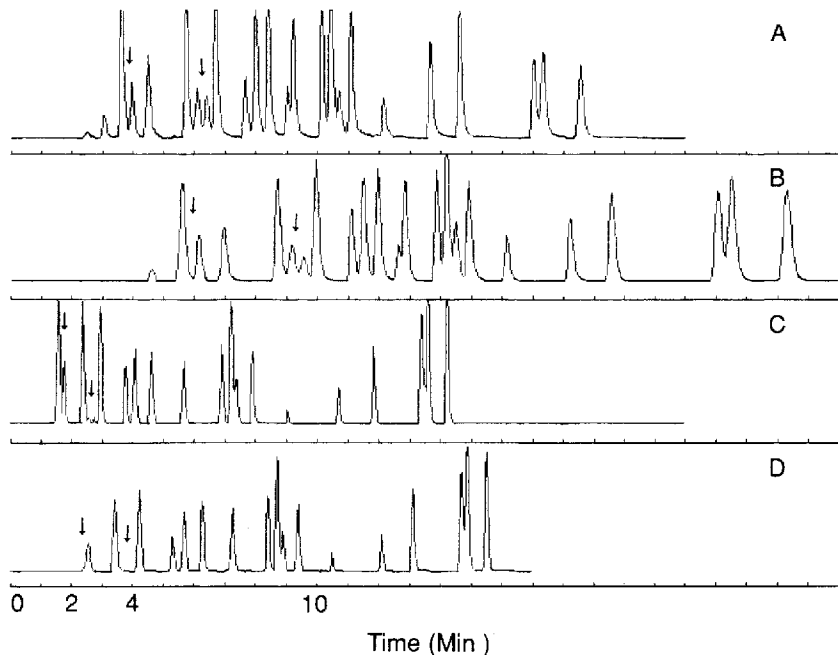


Fig. 2. Comparison of the effect of nitrogen flow-rates on method 601 analysis using EICD. (A) 0.53 mm I.D. capillary, 15 ml/min nitrogen; (B) 0.53 mm I.D. capillary, 15 ml/min nitrogen; (C) 0.32 mm I.D. capillary, 15 ml/min nitrogen; (D) 0.32 mm I.D. capillary, 8 ml/min nitrogen.

equately resolve 39 compounds, including the dichlorobenzenes, in 27 min or the seven 602 compounds in 15 min by use of 0.53 mm I.D. columns. While the chromatographic performance of the 0.53 mm I.D. column was similar to the 0.75 mm I.D. capillary it had the sturdiness of fused silica.

In the present paper, we extended the study to 0.32 mm I.D. capillary columns and investigated the effects of carrier gas type and flow-rate in order to optimize the conditions. A typical chromatogram of EPA 601/602 with EICD and PID on an 0.53 mm I.D. capillary with nitrogen as the carrier gas is shown in Fig. 1. In Fig. 2, the results obtained with EICD on 0.53 and 0.32 mm I.D. columns at high and low flow-rates are compared. With nitrogen, low flow-rates do not improve resolution even with high boiling compounds while a number of volatiles are lost at 6–8 ml/min on both columns, presumably because of inadequate sweeping of the trap. Similar results were observed for PID as shown in Fig. 3.

The effect of carrier gas is shown in Fig. 4 for both the 0.53 and 0.32 mm I.D. columns. With the 0.32 mm I.D. capillary, helium dramatically increased the tailing seen with EICD although no such effect was observed with PID. With the 0.53 mm I.D. column, no significant increase in tailing was observed when the helium was replaced by nitrogen. The low flow-rate of nitrogen (6 ml/min) caused some loss of the volatiles in the early eluting peaks of the chromatogram. At the same time, these volatiles were observed with helium at 6 ml/min. For both the 0.32 and 0.53 mm I.D. columns, flow-rates of 15 and 8 ml/min, respectively, provide optimum results with nitrogen and helium respectively.

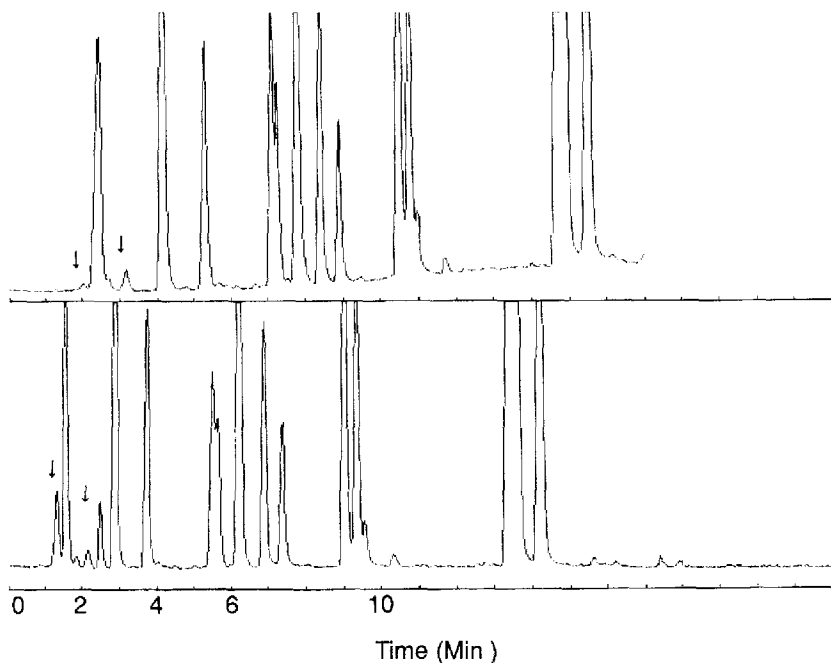


Fig. 3. Comparison of the effect of nitrogen flow-rate on method 602 analysis using PID and a 0.32 mm I.D. capillary. (Top) 8 ml/min nitrogen; (Bottom) 15 ml/min nitrogen.

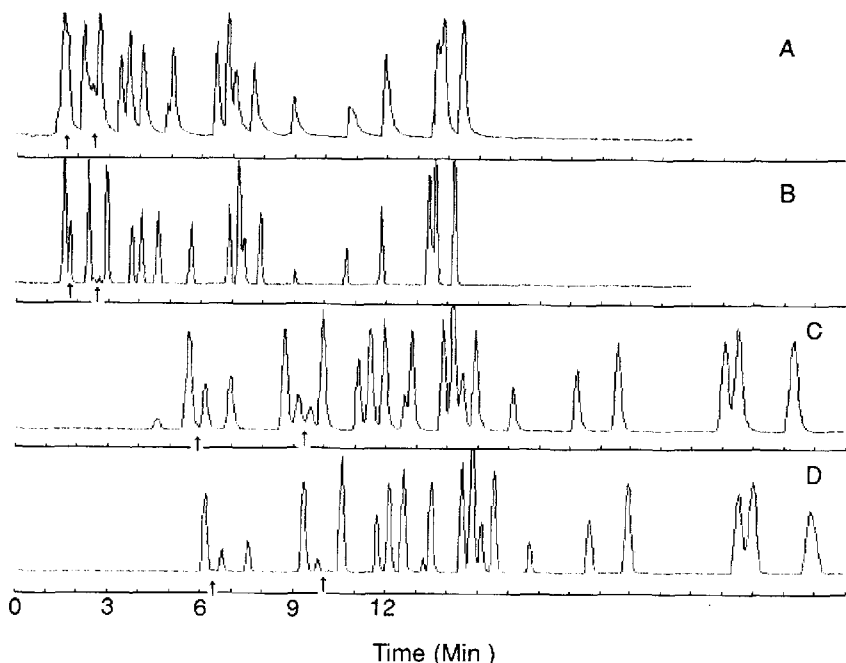


Fig. 4. Comparison of the effect of helium and nitrogen carrier gas on method 601 analysis using EICD. (A) 0.32 mm I.D. capillary, 15 ml/min helium; (B) 0.32 mm I.D. capillary, 15 ml/min nitrogen; (C) 0.53 mm I.D. capillary, 6 ml/min helium; (D) 0.53 mm I.D. capillary, 6 ml/min nitrogen.

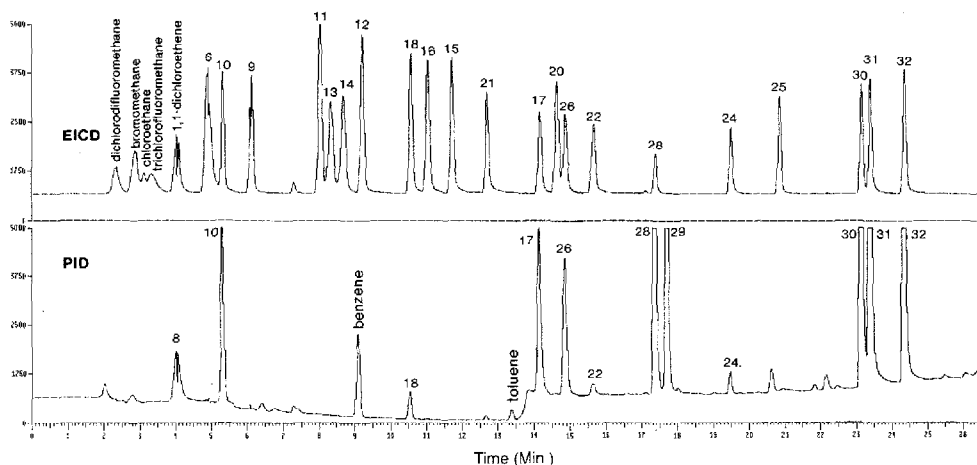


Fig. 5. Capillary chromatograms of volatiles with silica gel in trap. Conditions: capillary column; flow-rate, 8 ml/min; helium carrier gas; temperature, 35°C, hold for 5 min, then from 35 to 140°C at 5°C/min, hold at 140°C for 5 min; EPA method 601 trap.

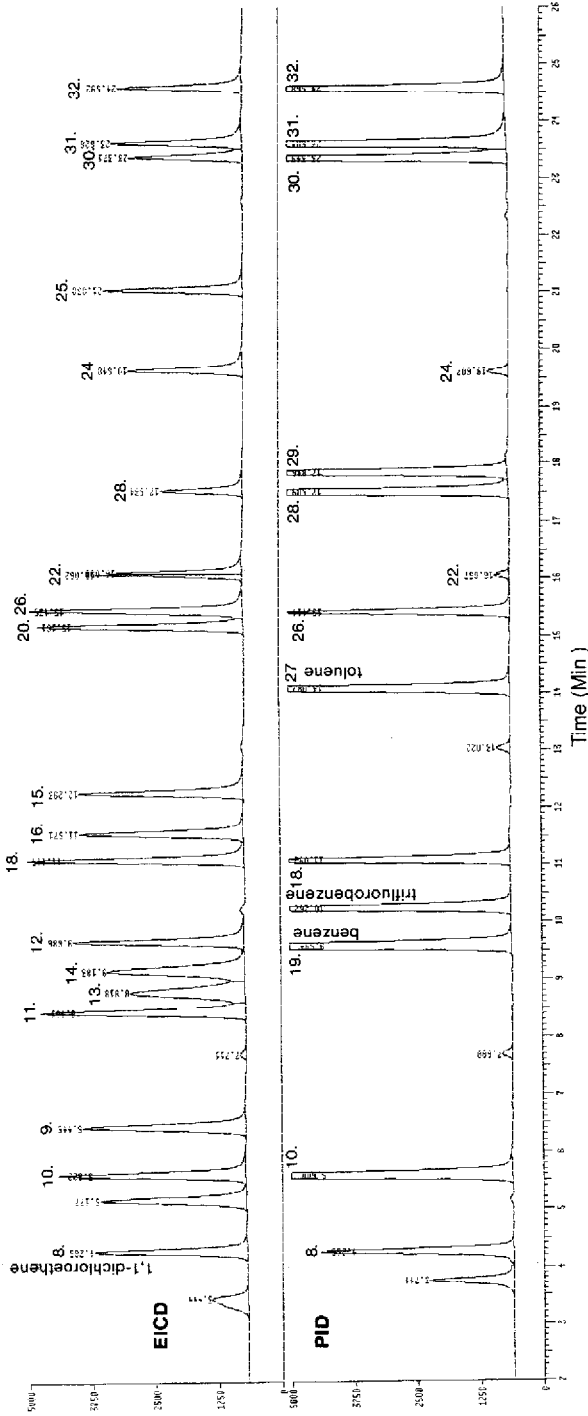


Fig. 6. Capillary chromatograms of volatiles without silica gel in trap. Conditions as for Fig. 5.

EPA method 502.2, one of the first methods with capillary columns, requires a starting temperature of 10°C below ambient for the analysis. The chromatogram in Fig. 5 indicates that the four common volatiles that we selected for our study are well resolved at an initial temperature of 35°C without the need for low temperatures. With this column and conditions, we encountered some problems with the system integration. Methods 601 and 602 as written require different columns and detectors. Our goal with capillary columns was to use a single column with the electrolytic conductivity detector in series with the photoionization detector. The operating conditions for the volatiles require silica gel in the trap (purge-and trap) to retain the volatiles. However, with silica gel in the trap, the dry-purge cycle does not adequately remove the water, and the resulting high concentration of water in the detector reduces the response of the PID to benzene and toluene. The negative peak starting at *ca.* 2 min and continuing to 14 min in Fig. 6 is the result of the high water content

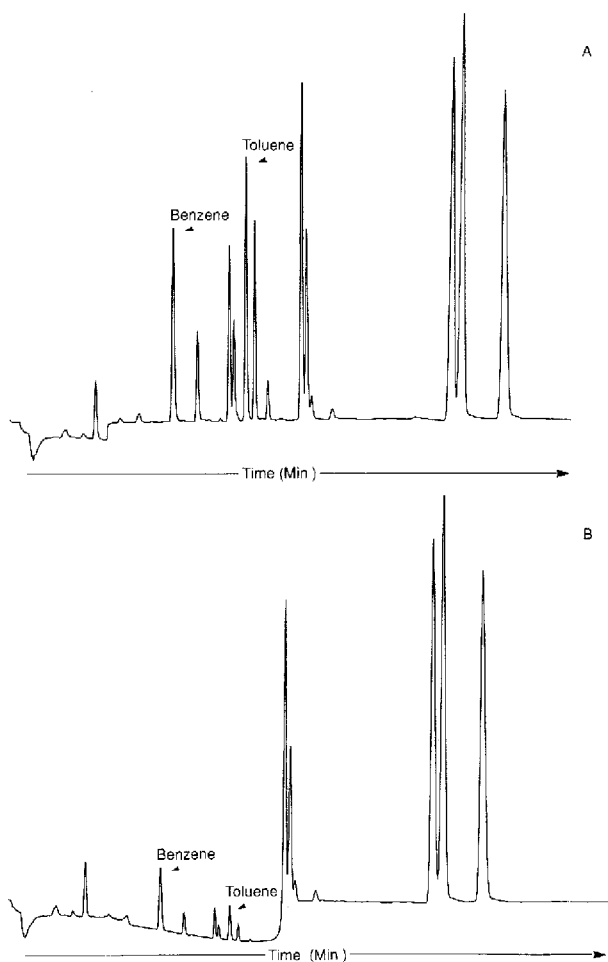


Fig. 7. Capillary chromatograms of volatiles with silica gel and (A) 2 and (B) 4 min purge cycles.

in the PID cell. When the silica gel trap was eliminated (Fig. 6), the volatiles were not detected, but the PID baseline was flat and the benzene and toluene peaks were off-scale. Suspecting that the purge cycle could be modified to eliminate this quenching effect of water, we reduced the purge cycle from 4 to 2 min. The quenching effect of water on the benzene and toluene response was thereby eliminated as shown in Fig. 7. By reducing the purge cycle on the purge-and-trap to 2 min, we are able to determine the volatiles by EICD without any interference by water in PID. There was no indication of loss of sensitivity or inefficient desorption with the shorter desorption times. Thus, the conversion of packed to capillary columns can now be successfully accomplished.

CONCLUSIONS

The 0.53 or 0.32 mm I.D. capillary columns produce efficient separation of all 36 EPA 601/602 compounds. If nitrogen was used as the carrier gas, 15 ml/min provides the best results in terms of efficiency and retention of the more volatile species. With helium as the carrier gas, 6–8 ml/min provides optimum results although noticeable tailing is observed with the 0.32 mm I.D. capillary column. The long purge cycle specified by EPA should be changed from 4 to 2 min to eliminate the water interference. In that way, volatile hydrocarbons (b.p. < 35°C) can be analyzed without the need for low temperatures.

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