

Analysis of Purgeable Organics in Water by Capillary GC/PID-EICD

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Abstract

Some aspects involved in converting U.S. Environmental Protection Agency (EPA) Methods 601 and 602 to the use of capillary columns instead of packed columns is discussed. The conversion optimizes the methods so that a photolization detector (PID) and an electrolytic conductivity detector (EICD) can be run in series. Also discussed is a modification of Method 602 to permit the analysis of aromatics in gasoline-contaminated groundwater samples that contain significant quantities of alkanes. The substitution of a 530- μ m fused-silica capillary column for a packed column results in improvements in resolution, sensitivity, speed of analysis, and reliability.

Introduction

In the early 1970s, Congress passed the Clean Water Act. This required the EPA to develop methodology for the analysis of 119 organics in water normally termed priority pollutants. Due to time and manpower constraints, the methodology selected was gas chromatography/mass spectrometry (GC/MS). Although GC/MS could provide data on all the priority pollutants, it is a complex and costly technique that requires a highly skilled individual for operation. It was clear that other methods would have to be developed if routine monitoring was to be conducted by a large number of laboratories, a necessary prerequisite for a successful program.

As a result, shortly after the first standards on GC/MS were issued, work began at the EPA Water Labs in Cincinnati, Ohio on alternative methods based on GC (with a variety of detectors) and liquid chromatography (LC) that were simpler, but not as broadly applicable as the MS methods. Because many of the methods were for low molecular weight hydrocarbons which are easily lost by direct injection, a purge-and-trap technique was developed for analysis of these "purgeable pollutants" (1). This resulted in a series of methods for the analysis of organics in industrial discharges designated by the U.S. government as Methods 601-613, 624, 625, 1624, and 1625. Recently, these methods have been described in detail in the Federal Register (2).

Twelve of these proposed methods involve GC or LC, and three of the proposed alternate methods require GC/MS. In

this paper, the primary concern is with EPA methods for purgeables, which include Methods 601 (halocarbons, 29 compounds), 602 (aromatics, 7 compounds), and the corresponding 500 series methods for drinking water.

The Federal Register (3) specifies the HNU photoionization detector (PID) or equivalent in Method 602 for industrial discharges and in Method 503.1 for drinking water. Since the 600 series methods were developed in the late 1970s and early 1980s, the separation technology is based primarily on packed columns. In 1979, Dandeneau and his colleagues (4) described a new type of capillary column based on fused-silica glass tubing rather than the more commonly used soda lime or borosilicate glasses. They used a polyimide coating on the outside of the column to provide support, protection, and flexibility. The result was a revolution in capillary column development. The resulting columns were very rugged and yet flexible and much easier to handle and install into the GC, thereby extending the usefulness of these columns beyond the very skilled practitioner to the normal QC or laboratory chemist. An added advantage of these columns was the inertness of the fused-silica surface compared to other glasses, which further extended the range of applications for these columns. Although capillary columns were widely used in the late 1970s in Europe (>70% in many countries), only 15% of the GCs in the United States were equipped with capillary columns at that time. This rose to 50% by the mid 1980s due primarily to the introduction of fused-silica capillary columns (5). Now, with the recent upsurge in interest in capillary columns, a considerable effort is underway at the EPA to convert the current packed column methods to include the use of capillary columns (6).

This paper will be concerned with some of the aspects involved in the conversion of methods for packed columns to capillary columns (e.g., Methods 601 and 602) optimizing the methods such that the PID (nondestructive) and the electrolytic conductivity detector (EICD) can be run in series. A modification of Method 602 to permit the analysis of aromatics in gasoline-contaminated groundwater samples that contain significant quantities of alkanes is also presented.

Experimental

Results were carried out on HNU Models 321 and 421 GCs (HNU Systems) equipped with an integral HNU PID (10.2 eV lamp), a Model 4420 EICD (OI Corp.), an OI Model 4460 purge-

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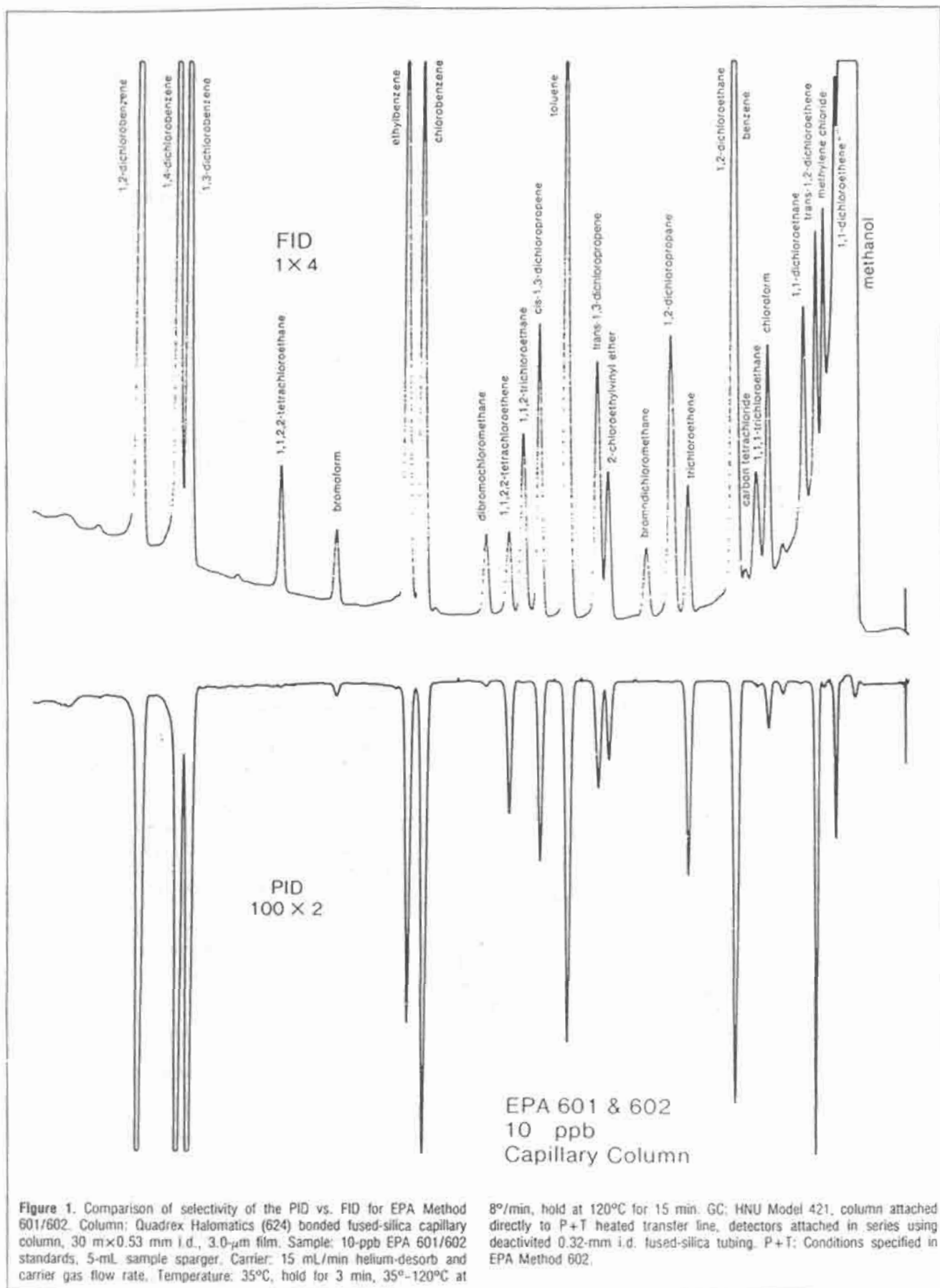


Figure 1. Comparison of selectivity of the PID vs. FID for EPA Method 601/602. Column: Quadrex Halomatics (624) bonded fused-silica capillary column, 30 m \times 0.53 mm i.d., 3.0- μ m film. Sample: 10-ppb EPA 601/602 standards, 5-mL sample sparger. Carrier: 15 mL/min helium-desorb and carrier gas flow rate. Temperature: 35 $^{\circ}$ C, hold for 3 min, 35 $^{\circ}$ -120 $^{\circ}$ C at

8 $^{\circ}$ /min, hold at 120 $^{\circ}$ C for 15 min. GC: HNU Model 421, column attached directly to P+T heated transfer line, detectors attached in series using deactivated 0.32-mm i.d. fused-silica tubing. P+T: Conditions specified in EPA Method 602.

and-trap, and an OI universal autosampler. The OI purge-and-trap system has a built-in dry purge accessory as a standard feature. The dry purge is a necessity when utilizing a PID. If this mode is not used, the negative peak resulting from the quenching effect of water in the PID can mask early eluting peaks. This phenomenon is particularly evident on low level samples. The autosampler holds 27 standard 40 cc VOA EPA vials, eliminating the need to manually transfer the sample from the collection vial to the purging vessel. The data was collected on a Spectra Physics Model 4270 integrator and a strip chart recorder. Prepurified nitrogen (packed columns) and helium (capillary columns) were used as both the carrier gas for the GCs and for the purge gas for the purge-and-trap. All chemicals were ACS grade or equivalent. The 601 and 602 standards were obtained from Supelco. The 0.53-mm, 624 Halomatics (3.0 μ m film) capillary column was purchased from Quadrex Corp. The column packings specified in EPA Methods 601 and 602 (packed column methods) were obtained from Supelco. These materials were packed in (6 and 8 ft \times 0.1 in.) stainless steel, as prescribed in the Federal Register (3).

The columns used for the determination of aromatic hydrocarbons in gasoline contaminated samples were a 530- μ m, DB-5 (1.0- μ m film) for the PID and a 530- μ m, DB-Wax (1.0- μ m film) obtained from J&W Scientific. The GC was an HP 5890 (Hewlett-Packard) equipped with a Model PI 52-02A PID (HNU Systems).

Results and Discussion

The PID (10.2 eV) was chosen over the flame ionization detector (FID) by the EPA (3) mainly because of its improved selectivity (7). The PID will not respond to low molecular weight chloroalkanes commonly found in water samples (these species have ionization potentials greater than 11 eV), whereas the FID will. Selectivity can be seen in Figure 1 where the PID responds only to the aromatics, chloroaromatics, and chloroalkenes. The FID responds to more than 30 compounds, including methanol in which the standards are made up. The large tailing methanol peak, which is not observed on the PID (IP of methanol is 10.9 eV) or the EICD when used, is found to obscure some of the earlier eluting compounds. Note also the difference in sensitivity for the PID (100 \times) and the FID (1 \times). The lower sensitivity results in a poorer chromatogram with a large solvent response and considerable baseline drift that is not observed on the PID.

One of the first modifications of EPA methods made at HNU was the incorporation of the EICD in series downstream of the PID. This eliminated the need for two separate chromatographic analyses and was found to quickly detect an improperly functioning detector based on an expected response ratio for a given quantity of component on each detector. A typical packed column chromatogram for EPA-601 and 602 compounds is shown in Figure 2 (identification of the peaks is listed in Table I). One limitation noted with the packed column method was that a number of components were unresolved: 1,1,2-trichloroethane, *trans*-1,3-dichloropropane, dibromochloromethane, 1,1,2,2-tetrachloroethane, and 1,1,2,2-tetrachloroethane. By utilizing a capillary column for this analysis, the compounds that coeluted on the packed column could be completely resolved on the 30-m \times 0.53-mm i.d. capillary column. Under certain chromatographic conditions, benzene and 1,2-dichloroethane will coelute, but the former is not detected by the EICD and the latter is not detected by PID thus providing the capability

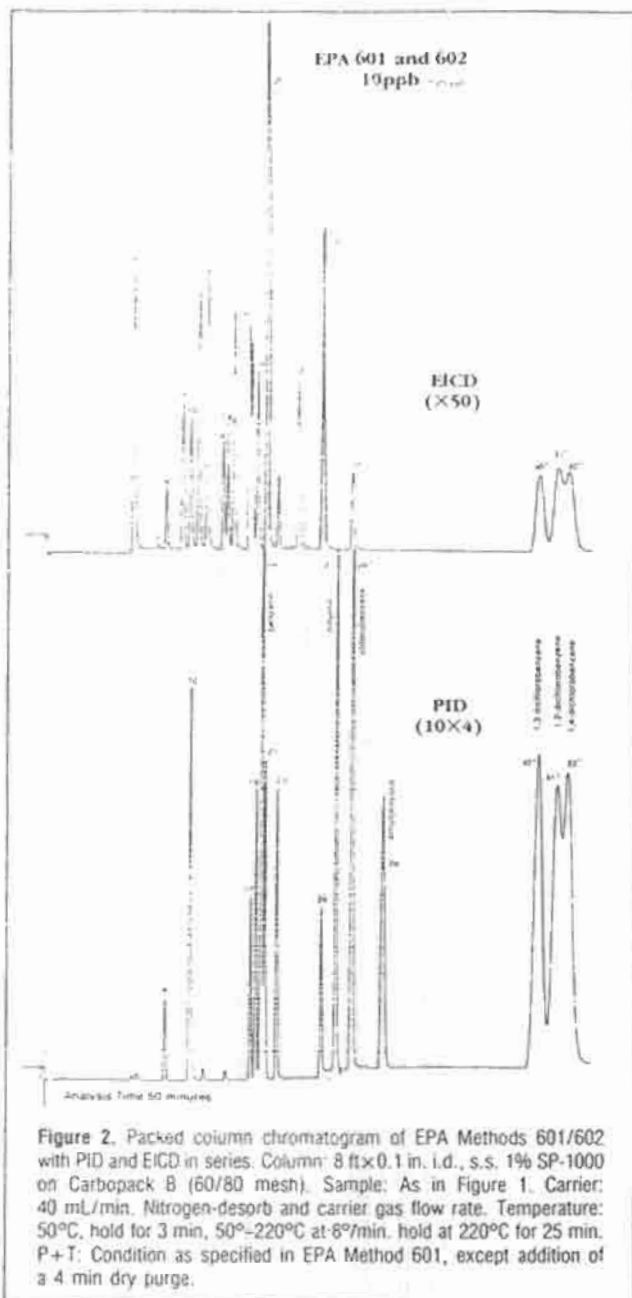


Figure 2. Packed column chromatogram of EPA Methods 601/602 with PID and EICD in series. Column: 8 ft \times 0.1 in. i.d., s.s. 1% SP-1000 on Carbopack B (60/80 mesh). Sample: As in Figure 1. Carrier: 40 mL/min. Nitrogen-desorb and carrier gas flow rate. Temperature: 50°C, hold for 3 min, 50°–220°C at 8°/min, hold at 220°C for 25 min. P+T: Condition as specified in EPA Method 601, except addition of a 4 min dry purge.

Table I. Peak Identification for Figures 2 and 3.

Peak number	Peak number		
1	Chloromethane	17	<i>cis</i> -1,3-Dichloropropene
2	Bromomethane	18	Trichloroethene
3	Vinyl chloride	19	Benzene
4	Dichlorodifluoromethane	20	1,1,2-Trichloroethane
5	Chloroethane	21	<i>trans</i> -1,3-Dichloropropene
6	Methylene chloride	22	Dibromochloromethane
7	Trichlorofluoromethane	23	2-Chloroethylvinyl ether
8	1,1-Dichloroethane	24	Bromoform
9	1,1-Dichloroethane	25	1,1,2,2-Tetrachloroethane
10	<i>trans</i> -1,2-Dichloroethane	26	1,1,2,2-Tetrachloroethane
11	Chloroform	27	Toluene
12	1,2-Dichloroethane	28	Chlorobenzene
13	1,1,1-Trichloroethane	29	Ethylbenzene
14	Carbon tetrachloride	30	1,3-Dichlorobenzene
15	Bromodichloromethane	31	1,2-Dichlorobenzene
16	1,2-Dichloropropane	32	1,4-Dichlorobenzene

to quantitate each compound. The separation of these species on a Supelco VOCOL (750 μm i.d.) column has previously been reported by the present authors (8).

The use of detectors in series has the added advantage of compound or class identification as shown by Driscoll et al. (9) and Cox et al. (10). Cox evaluated capillary PID/FID for volatile organic compounds from waste water treatment facilities. Using PID/FID ratios, they were able to classify all sample compounds into chemical classes with some level of confidence. They obtained >80% species identification for 76% of the air samples and 26% of the water samples. Cox's data clearly indicates the potential of this technique: it is easier to use, cheaper than GC/MS, and has the potential for high sample throughput. PID/EICD may have been a better technique for the water samples because of the preponderance of chlorinated hydrocarbons. This detector may have improved their percentage of class identification for waste water samples.

A 530- μm fused-silica column was used for all analyses. These columns have been shown to easily replace packed columns (11) as they can be used at relatively high column flow rates (5 to 30 cc/min), can easily be installed into most packed column instruments, and yet still provide considerably more plates and separation capability than a packed column. A typical chromatogram of 601 and 602 compounds on a fused-silica column is shown in Figure 3. In addition to the improved resolution of the capillary column, virtually none of the components coelute, the speed of analysis is greatly increased (50 min vs. 25 min) as seen when Figures 2 and 3 are compared, and an improvement in sensitivity of nearly one order of magnitude for the PID is realized. This latter item is partially the result of the lower flow rate required with the fused-silica column, and for concentration sensitive detectors, such as the PID, the sensitivity is proportional to the reciprocal of the flow rate (e.g., $S = 1/F$, where S is the sensitivity and F is the detector flow rate). In addition, the shortened retention times and sharper peaks obtained on the capillary column further improves the sensitivity of this system. All of these benefits were found to improve the minimum detection limits for these compounds. A schematic of the system is shown in Figure 4.

In many cases, only the 602 aromatic compounds need to be analyzed. Here the analysis time can be reduced from the 27 min on the EPA specified packed column to 15 min on the Halomatics capillary column as indicated in Figures 5a and 5b.

For groundwater analyses in the vicinity of gasoline stations, it is necessary to measure levels of aromatic hydrocarbons to indicate the presence of gasoline or fuel oil contamination in these samples. EPA Methods 602 and 8020 do not have adequate selectivity for this particular analysis because high molecular weight alkanes can coelute with the aromatic hydrocarbons resulting in an interference.

There are in excess of 250,000 gasoline stations in the United States. It is estimated that 30 to 40% of these stations have leaking fuel storage tanks contributing significantly to the problem of ground water contamination. The need for a reliable and accurate method is essential. One approach (13) involved the use of a highly polar, 530- μm capillary column that would elute the nonpolar alkanes quickly (and in one broad peak) while providing adequate resolution for the aromatic hydrocarbons, particularly the xylenes. An added feature of this method is that alkanes and aromatics can be quantitated, if desired. The polar liquid phase selected for the analysis was a Carbowax bonded DB-Wax. A difficulty encountered was the injection of residual water from the purge-and-trap that led to a stripping of the

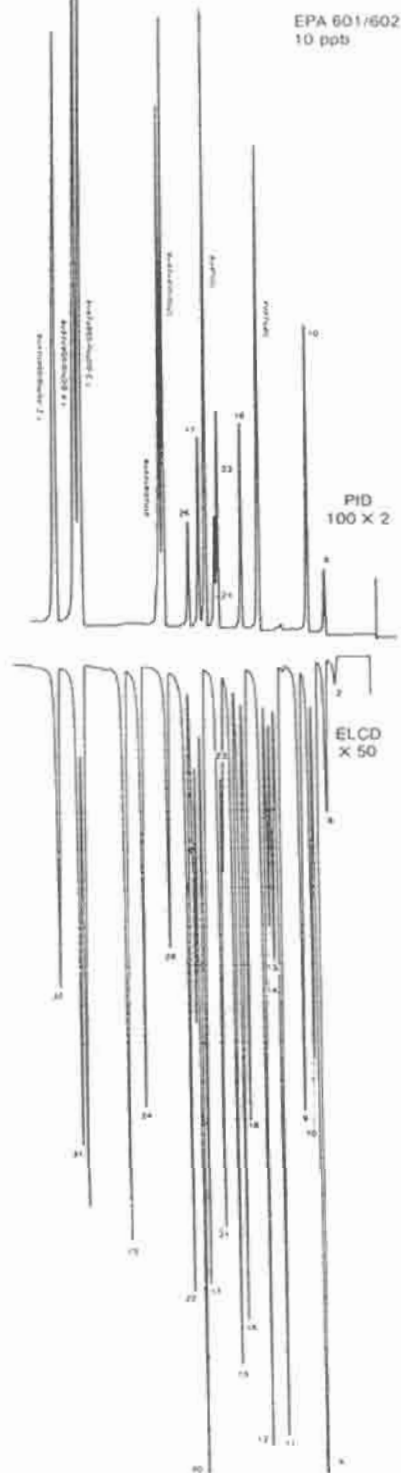


Figure 3. Capillary chromatogram of EPA methods 601/602 with PID and EICD in series. All conditions as in Figure 1. GC: HNU Model 321. Analysis time: 25 min.

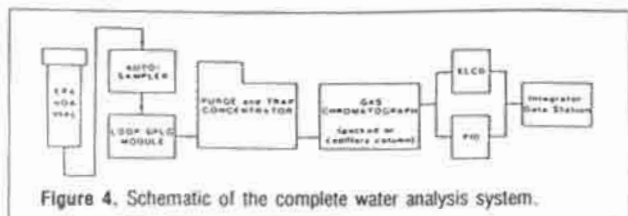


Figure 4. Schematic of the complete water analysis system.

Carbowax and subsequent degradation of the PID sensitivity. The typical change in sensitivity with time is shown in Figure 6A. A second capillary column from a different manufacturer lasted for six weeks or more without decay on the PID (no apparent bleed), but the column resolution appeared to degrade at the end of that time. There may have been some kind of buildup in the column which caused the poorer resolution, but the cause has not yet been determined. As indicated above, the

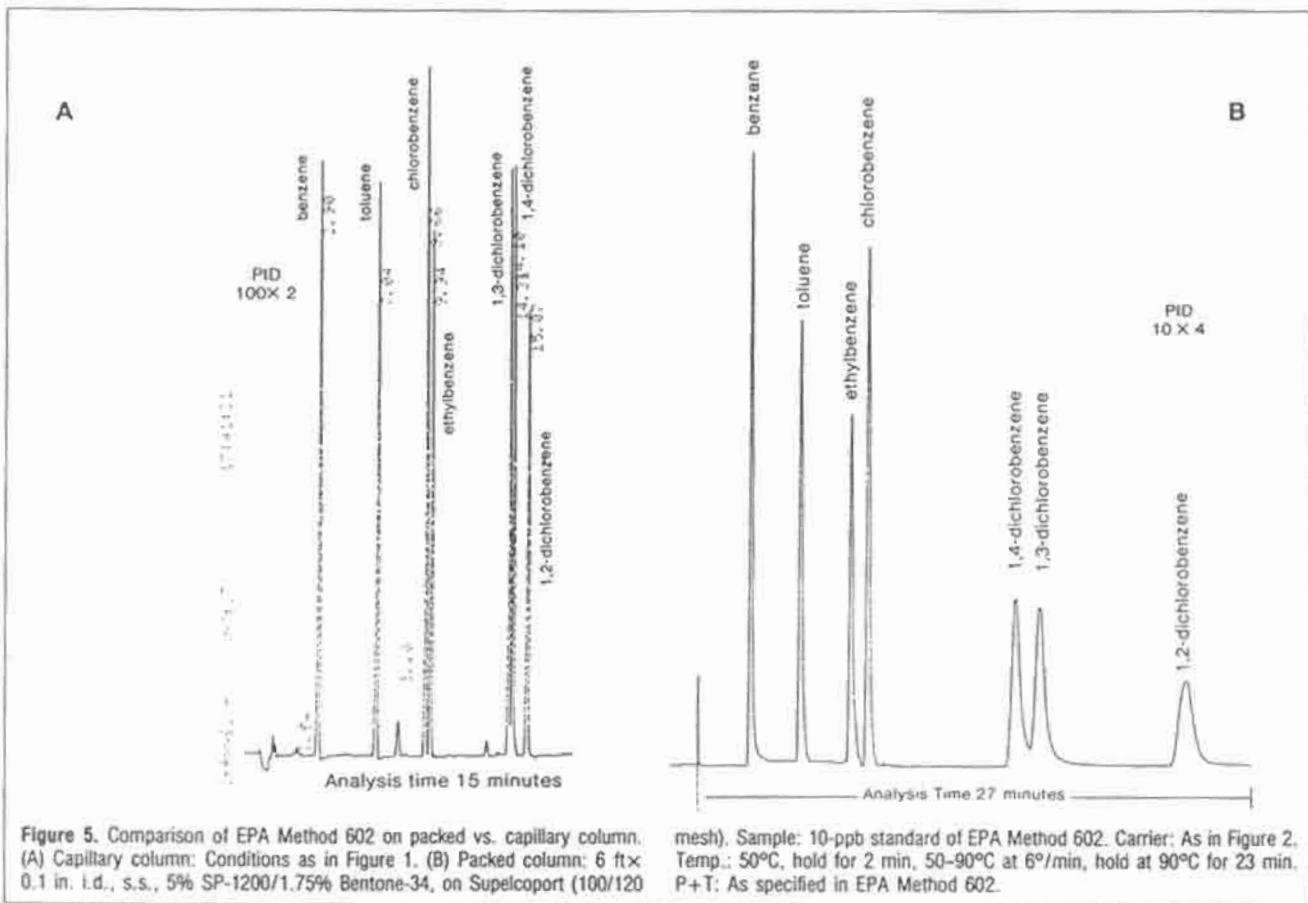


Figure 5. Comparison of EPA Method 602 on packed vs. capillary column. (A) Capillary column: Conditions as in Figure 1. (B) Packed column: 6 ft x 0.1 in. i.d., s.s., 5% SP-1200/1.75% Bentone-34, on Supelcoport (100/120

mesh). Sample: 10-ppb standard of EPA Method 602. Carrier: As in Figure 2. Temp.: 50°C, hold for 2 min, 50-90°C at 6°/min, hold at 90°C for 23 min. P+T: As specified in EPA Method 602.

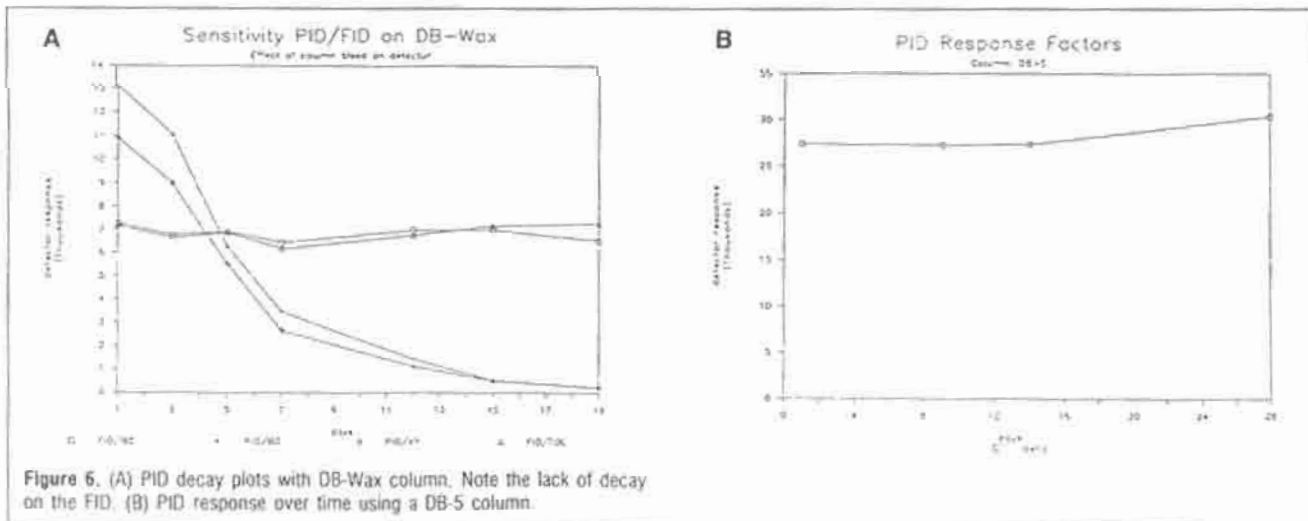


Figure 6. (A) PID decay plots with DB-Wax column. Note the lack of decay on the FID. (B) PID response over time using a DB-5 column.