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## POTENTIAL PROBLEMS WITH THE USE OF DISTILLED WATER IN PESTICIDE RESIDUE ANALYSES\*

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## SUMMARY

Precautions should be taken with distilled water that may be included in any scheme of analysis for pesticides, especially in the nanogram–picogram analytical range, to insure that the water has not been contaminated with organic components derived from the water distillation system. Ultimate analysis of the sample by gas chromatography, utilizing an electron capture detector, will record any contaminants present and they may confuse the interpretation of the pesticide analytical data. Preferably, an all-glass still unit which contains no plastic fittings of any type should be used. Some of the potential problems with distilled water that may occur if plastic or resin components are included in the distillation system are discussed in this report.

## INTRODUCTION

There are occasions when distilled water is included in the preparation and extraction of a sample for the isolation of a pesticide residue. For example, water may be used in an aqueous salt solution to prevent emulsification problems in an aqueous–organic solvent partition step; or aqueous acidic and basic solutions may be used to adjust the pH of the mixture; or an excess amount of water may be added to an acetonitrile–petroleum ether sample extract or an isopropanol–hexane soil extract to remove either the acetonitrile or isopropanol component from the respective mixtures; or distilled water may be used to equilibrate chromatographic adsorbents.

A casual observation of the many water-still systems on this University campus suggested possible contaminant problems with the distillate from such systems; that is, some of the systems included ion-exchange resin filters encased in polyvinyl chloride containers; all-glass systems contained teflon fittings, and many of the units included some type of plastic tubing in their water dispensing system. The analyst has become increasingly cognizant of the possible misinterpretation of the analytical data when, for example, polychlorobiphenyls derived from plastic materials may be

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mistakenly identified as chlorinated pesticides. In addition to the pesticide chemist, the microbiologist, zoologist, and other researchers in related areas, should be concerned about such organic contaminants in a seemingly pure distilled water medium which, if present, may (or may not) provide an undesirable toxic factor to the organism under study. Obviously, to avoid such potential problems, the quality and purity of a researcher's distilled water supply should be determined and safeguards should be initiated to eliminate any potential problems.

Distilled water samples were obtained from various water-still systems situated on the main campus of this University and examined for possible contaminants responsive to gas chromatograph analysis utilizing an electron capture detector. The effect of the presence of teflon and resin components on the quality of distilled water was also examined. Also, distilled water was prepared from an all-glass system for comparative purposes. The procedural details and the results of the study are the substance of this report.

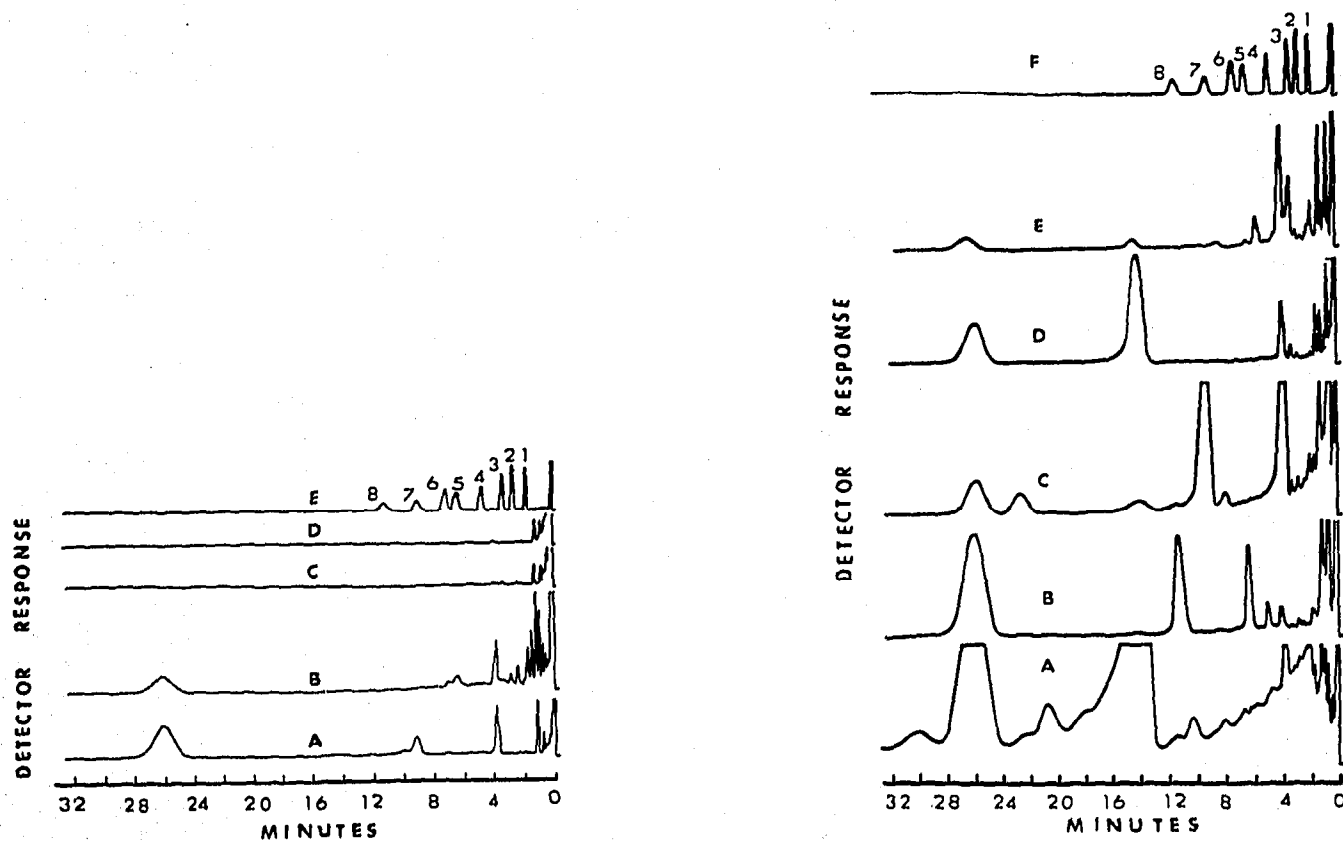


Fig. 1. Gas chromatograph curves of electron-capture-detector sensitive components in samples obtained from (A) distilled water, Barnstead still Unit No. 1; (B) distilled water, Barnstead still Unit No. 2 (see text, Experimental); (C) local tap water; (D) nanograde hexane reagent blank; (E) pesticide standards, (1) lindane 0.06 ng; Nos. 2, 3, 4, 5, 6, 7, 8 are heptachlor, aldrin, heptachlor epoxide, DDE, dieldrin, DDD, *p,p'*-DDT, respectively, each 0.12 ng.

Fig. 2. Gas chromatograph curves of electron-capture-detector sensitive components in water samples obtained from (A) glass-distilled water stored in rubber-stoppered reservoir; (B) tap water passed through a mixed bed ion-exchange resin cartridge (resin encased in a polyvinyl chloride container); (C) glass-distilled water, Unit No. 5; (D) glass-distilled water, Unit No. 4; (E) glass-distilled water, Unit No. 3 (for description of Unit Nos. 3, 4, and 5, see text, Experimental); (F) pesticide standards, (1) lindane 0.12 ng; Nos. 2, 3, 4, 5, 6, 7, 8 are heptachlor, aldrin, heptachlor epoxide, DDE, dieldrin, DDD, *p,p'*-DDT, respectively, each 0.24 ng.

## EXPERIMENTAL

*Description of water-still systems*

*Unit No. 1.* Barnstead still, tin-lined unit, with a tygon tubing connection to the reservoir and a rubber tubing delivery system. (See Fig. 1).

*Unit No. 2.* Barnstead still, tin-lined unit, with a tygon tubing delivery system (See Fig. 1).

*Unit No. 3.* Glass still (Corning commercial design unit) with teflon stopcock outlet. The tap water passed through a mixed bed ion-exchange resin column prior to entering the still system. Rubber tubing was a part of the delivery system (See Fig. 2, curve E).

*Unit No. 4.* Glass still (Kontes commercial design unit) with teflon tubing fittings. No rubber or other plastic tubing was present in this system (See Fig. 2, curve D).

*Unit No. 5.* Glass still (Kontes commercial design unit) with teflon tubing fittings. The tap water passed through a mixed bed ion-exchange resin column prior to entering the still system. No rubber or other plastic tubing was present in this system (see Fig. 2, curve C).

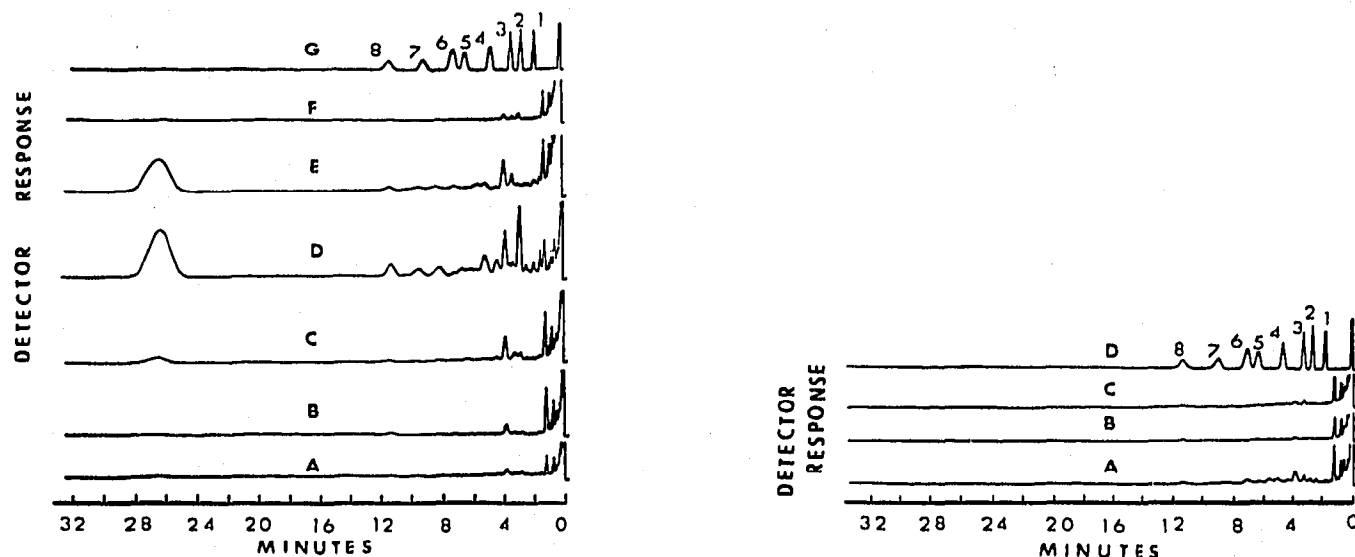


Fig. 3. Gas chromatograph curves of electron-capture-detector sensitive components in samples obtained from (A) residual water in still boiling pot containing teflon stopcocks; (B) residual water in still boiling pot containing teflon stirring bars; (C) water distilled in presence of teflon stirring bars; (D) water distilled in presence of teflon stopcocks (see text, Supplementary Experiments, item Nos. e and f); (E) hexane-extracted teflon stopcock; (F) hexane-extracted teflon cap liner (see text, Supplementary Experiments, item Nos. c and d); (G) pesticide standards, (1) lindane 0.06 ng; Nos. 2, 3, 4, 5, 6, 7, 8 are heptachlor, aldrin, heptachlor epoxide, DDE, dieldrin, DDD, *p,p'*-DDT, respectively, each 0.12 ng.

Fig. 4. Gas chromatograph curves of electron-capture-detector sensitive components in samples obtained from (A) a composite 3000 ml water distillate from 16,200 ml tap water from an all-glass still system (see text, Procedure, paragraph [c]); (B) residual tap water in still boiling pot from distillate curve C; (C) water distillate of 2500 ml from 2600 ml of tap water from an all-glass still system (see text, Procedure, paragraph [b]); (D) pesticide standards, (1) lindane 0.06 ng; Nos. 2, 3, 4, 5, 6, 7, 8 are heptachlor, aldrin, heptachlor epoxide, DDE, dieldrin, DDD, *p,p'*-DDT, respectively, each 0.12 ng.

*Unit No. 6.* All-glass still system (Control unit), which included a 3-l, 3-neck, ground-glass joints, Pyrex round bottom boiling flask connected to a Friedrichs condenser. The entire system was soaked in cleaning solution (concentrated sulfuric acid-sodium dichromate) for 16 h, rinsed thoroughly, and then heated at 200° for 16 h prior to use. No rubber, tygon, teflon, or any other form of plastic tubing or connection was used in this system (See fig. 4, curves A and C).

### *Gas chromatograph*

Varian-Aerograph Model 204, electron capture detector;  $\frac{1}{8}$  in.  $\times$  6 ft. glass column containing 4% SE-30, 6% QF-1 silicones on Chromosorb W, HP, 80-100 mesh; column temperature, 190°; injector temperature, 210°; detector temperature, 200°; carrier gas, nitrogen; flow rate, 25 ml/min.

### *Procedure*

(a) Except as noted below, 3500 ml of each distilled water sample was collected in reagent bottles known to be free of any organic contaminants (the bottles had previously contained "Nanograde" hexane). Each bottle cap contained a teflon liner. Nanograde hexane (100 ml) was added to each sample and the bottle was rotated at high speed on a roller-type jar mill for 1 h. After mixing, the sample was allowed to stand until the hexane and water phases separated. Fifty milliliters of the hexane layer were removed from the bottle by means of a volumetric pipette and concentrated to a small volume in an all-glass flash evaporator; the concentrate was transferred to a calibrated centrifuge tube and the final volume was adjusted to 0.5 ml with the aid of a warm steam bath and a stream of nitrogen. Suitable aliquots, usually 10  $\mu$ l, were applied to the gas chromatograph. (Note: All glassware was heat treated at 200° for 16 h (ref. 1).)

(b) Tap water (2600 ml) was distilled in the all-glass control unit until 2500 ml of distillate was collected. The distillate and the residual 100 ml of tap water were each extracted with hexane and concentrated as described above (See Fig. 4, curves C and B).

(c) Tap water (2700 ml) was distilled in the all-glass control unit until 500 ml of distillate was collected. This procedure was repeated five additional times, until a combined distillate of 3000 ml was obtained from 16,200 ml of tap water. The hexane extraction and concentration procedures were the same as described above (See Fig. 4, curve A).

### *Supplementary experiments*

(a) Tap water (3500 ml) samples were extracted with hexane as described above (See Fig. 1, curve C).

(b) Tap water (3500 ml) was passed through a Barnstead mixed-bed ion-exchange resin cartridge and the deionized water was extracted with hexane as described above (see Fig. 2, curve B).

(c) A teflon bottle-cap liner (size no. 38, Chemical Rubber Co.) was soaked overnight (16 h) in 50 ml hexane (See Fig. 3, curve F).

(d) A teflon stopcock (weight 7 g) was soaked overnight (16 h) in 50 ml hexane (See Fig. 3, curve E). The hexane solutions of Nos. (c) and (d) were concentrated to a volume of 0.5 ml and examined by gas chromatography.

(e) Three new (previously unused) teflon stopcocks (weight 42 g) and 2500 ml tap water were placed in the boiling flask of the all-glass control still system and 2000 ml of distillate was collected and extracted with hexane as described above (See Fig. 3, curve D).

(f) Two new teflon stirring bars (weight 19 g) and 2200 ml tap water were placed in the boiling flask of the all-glass control still system and 2000 ml of distillate was collected and extracted with hexane as described above (See Fig. 3, curve C).

(g) The residual amounts of water remaining in the boiling flasks of above experiments (e) and (f) were each extracted with hexane as previously described. Each of the hexane extracts was concentrated to 0.5 ml and 10  $\mu$ l aliquots of the concentrates were applied to the gas chromatograph (See Fig. 3, curves A and B).

## RESULTS AND DISCUSSION

For comparison, the qualitative and quantitative electron capture detector response of some of the commonly used chlorinated pesticides are graphically illustrated in all the figures in the range of 0.06–0.24 ng. The gas chromatograph curve for the hexane reagent blank is illustrated in Fig. 1, curve D. The tap water available on this campus is practically free from organic contaminants when used in the amounts ordinarily required in extraction procedures (Fig. 1, curve C). However, it is noted that with the continuous collection of distillate (from the all-glass control system) from a tap water source of a volume ranging from 2500 ml to 16,000 ml an upward trend of contaminants sensitive to the electron capture detector is apparent (see Fig. 4, curves A and C). It is also apparent from Fig. 4, curve B that these components are volatile at the temperature of boiling water, they co-distill with the water, and no residual contaminants remain in the boiling pot. A comparison of the amounts of these contaminants with the pesticides standards curve (Fig. 4, curve D) would place such contaminants in the area of a fraction of the p.p.t. range.

Fig. 1, curves A and B, illustrate the quality of distilled waters obtained from two Barnstead still systems and indicate two possible sources of contamination, namely, an accumulation of volatiles from the raw water plus contamination from contact of the distilled water with plastic tubing connections.

Curves C, D, and E of Fig. 2 illustrate the quality of distilled water obtained from commercially designed glass stills. Curves C and E were from systems which included a mixed bed ion-exchange resin filtering unit prior to the distillation step. Curve D was from a similar commercial glass still system without the ion-exchange unit and it contained no plastic connections other than the teflon fittings furnished with the unit. Curve B of Fig. 2 is an example of tap water which had been passed through a mixed bed ion-exchange resin column only (the resins were encased in a polyvinyl chloride container). Curve A of Fig. 2 is an example of distilled water which had been stored in a reservoir train of three 2- $\frac{1}{2}$ -gallon pyrex bottles joined together by means of tygon tubing and rubber stoppers; obviously, such water is not even satisfactory for rinsing glassware.

Some teflon items must include in their composition, to a greater or lesser degree, some plasticizer components, and this is evident in Fig. 3. Curve F shows that teflon liners used in bottle closures are practically free from plasticizer contaminants. Curve E shows that teflon stopcocks, of the type used in burettes and separatory

funnels, are not wholly inert and do contain hexane-soluble contaminants sensitive to an electron capture detector. Curve D illustrates that the teflon stopcock contaminants may be steam distilled and will appear in the distilled water obtained from systems containing teflon components. The amounts of such contaminants would, of course, be related to the amounts of plasticizers present in a given teflon material. For example, teflon stirring bars indicated a much smaller amount of contaminants than the teflon stopcocks (See Fig. 3, curve C).

Curves A and B of Fig. 3 illustrate that the teflon contaminants were almost completely volatile and that the residual water in the boiling pot was practically free of this material. However, it is of interest to note that the characteristics of curves A and B are quite similar to the gas chromatograph curve F (Fig. 3) of the hexane-extracted teflon cap liner.

To summarize, distilled waters obtained from systems ordinarily found in the average laboratory will contain contaminants that could interfere with and confuse the interpretation of any gas chromatographic organic pesticide data obtained with an electron capture detector; this is especially true if the investigator is concerned with ng-pg amounts of pesticides and subsequently the data are reported in terms of the p.p.b. or p.p.t. range. Commercially designed all-glass still systems which contain teflon fittings may contribute electron-capture sensitive contaminants to the gas chromatographic pattern. The inclusion of any ion-exchange resins in the still system will contribute contaminants to the final distilled water product. Storage supplies of distilled water will accumulate increased amounts of contaminants if the storage system includes rubber stoppers and plastic tubing connections (See Fig. 2, curve A).

The first normal reaction of the experienced analyst will be to belittle or ignore gas chromatograph responses of pesticides or pseudo-pesticides that occur in the p.p.t. range in the sample. This attitude would most probably be correct for the control or regulatory chemist who is primarily concerned with pesticide residues at the p.p.m. level. However, in areas of research or in the newer areas of monitoring programs, such as the monitoring of natural waters from various origins, p.p.b. or p.p.t. quantities cannot be wholly ignored until the full significance of such amounts can be related or equated with all other factors including the biota, in a given body of water.

If distilled water is required in any part of the analytical procedure for pesticides, especially where the final data may be in the p.p.b. or p.p.t. range, the water should be prepared in an all-glass system which has been previously acid cleaned and heat treated. A maximum of 3 l distilled water should be collected (provided that the original tap water is low in organic material content), and it should not be stored for any lengthy period of time prior to use; larger quantities of distillate could increase, and therefore magnify, the amount of potential contaminants co-distilled from natural waters. The contaminant accumulation in the distillate of a given batch of water could, perhaps, be minimized if the first 100 ml of distillate was discarded. Preferably, the water should be triple-distilled and the boiling pot should contain an oxidizing agent, such as potassium permanganate.

#### REFERENCES

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