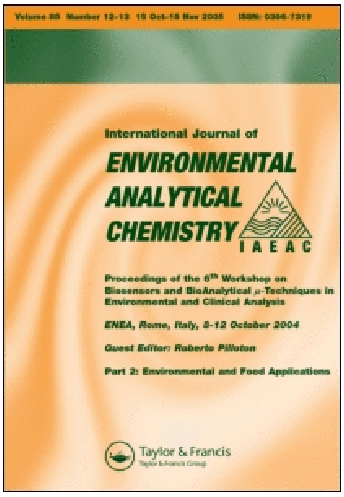

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# Simple Device for Isolation of Organic Compounds from Water

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# Simple Device for Isolation of Organic Compounds from Water

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A simple device for isolation of organic compounds from aqueous samples has been designed and its operating parameters tested during both periodic and continuous operation using isolation of organochlorine compounds as an example.

A stream of an aqueous sample is pumped at elevated temperature by a piston pump to an unit for expansion of the liquid phase surface, where the liquid is sprayed on the walls of the unit and flows down freely.

Organochlorine compounds passing to the gaseous phase are purged with a stream of purified air, oxidized and the chlorides formed are determined coulometrically. The designed device, due to its simplicity, can be built and employed in each averagely equipped laboratory.

KEY WORDS: Organochlorine compounds, water samples, coulometry, sample handling.

## INTRODUCTION

One of the basic analytical techniques used in the area of analysis of organic pollutants of various types of water (surface water, tap water, industrial effluents, etc.) is gas chromatography. The type of matrix represented by water causes limitations in maximum sample volume which can be directly introduced into a GC column. Usually, in the case of direct aqueous injection (DAI) this sample volume is on the order of several $\mu$l,[1] whereas in particular cases the injected aqueous sample does not exceed $400\,\mu$l.[2] Evidently, this order of magnitude of the analyzed sample determines unfavourable for trace analysis detection limit. Hence, in order to lower the detection limit it is necessary to introduce an additional step consisting in matrix exchange (other solvent or transfer of the analytes to the gaseous phase). This step can be accomplished by:

— liquid–liquid extraction;[3,4]
— adsorption on solid sorbents (sorbents of resin type and primarily Granular Activated Carbon—GAC) followed by liberation of trapped compounds by means of solvent or thermal desorption in a stream of inert gas;[5–8];
— membrane processes;[9–11];
— extraction of organic compounds from aqueous samples using a stream of suitable gas (air, nitrogen, argon, helium).

In this case such solutions of this problem as stripping (sparging)[12–14] or stripping combined with concentration of compounds from the gaseous phase (purge and trap technique),[15–17] closed loop stripping analysis—CLSA[18–20] and static or dynamic headspace—HS[21–24] can be distinguished. Certain modification of the latter technique is thin layer countercurrent headspace analysis—TLHS.[25]

Basic feature of all devices for isolation of organic compounds from aqueous sample utilizing both stripping and dynamic headspace is tendency for maximum expansion of the area of contact between gaseous and liquid phases at elevated temperature for possibly rapid extraction of organic compounds from liquid phase to a stream of gas.

The purpose of our investigations described here was design and determination of operational parameters of a simple device for isolation of organics from water. Generally, the device constructed can be classified as an apparatus utilized for dynamic headspace analysis.

## EXPERIMENTAL

### Apparatus

Figure 1 presents the design of a unit made of Pyrex glass for expansion of surface of the liquid phase using a spray technique. The unit had a total capacity of 0.9 l. A schematic diagram of an apparatus for isolation of organic compounds from aqueous solution is shown in Figure 2. About 400 ml of the solution is placed in a unit

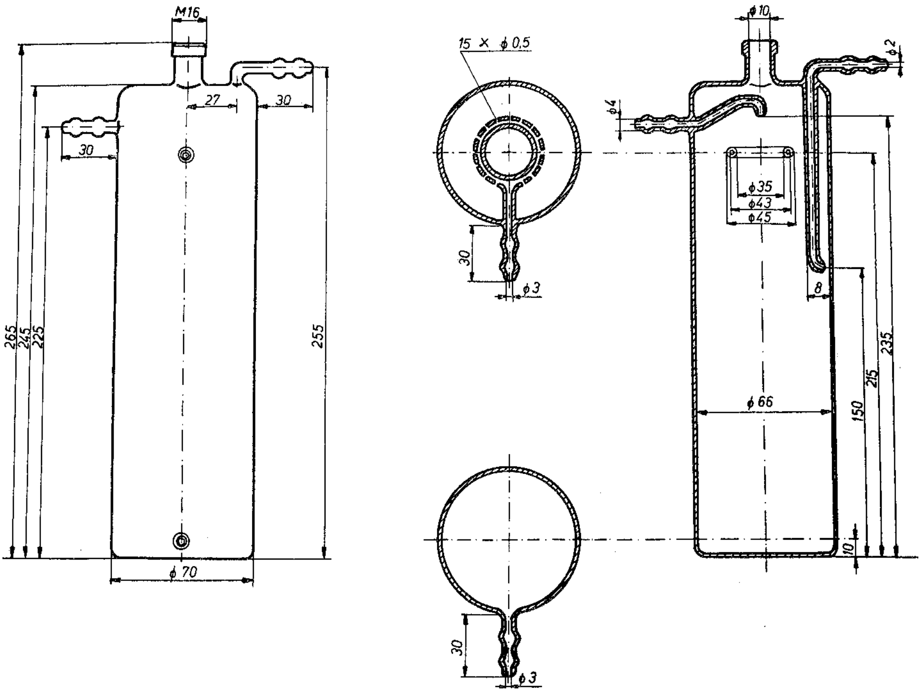

FIGURE 1 Unit of Pyrex glass for expansion of the liquid phase surface using a spray technique.

(1) from where it is pumped with a defined, regulated flow rate by means of a UNIPAN Poland model 336B automatic dispenser (3) and on reaching desired temperature in a heat exchanger (2) connected with a thermostat it is directed to the upper part of the unit (1). The sample is pumped via 15 holed jet of diameter 0.5 mm so that it flows a film down the upper internal wall of the unit. The entire unit can be thermostated but installation of an additional water jacket considerably complicates its construction. The heat exchanger sufficiently ensures constant temperature of the aqueous sample at the outlet of the holed jet. The described device was employed for isolation of organochlorine compounds. The compounds liberated from the liquid phase were purged from the unit (1) by means of a stream of purified air. Subsequently, they were combusted in an empty quartz tube heated to 950°C and the

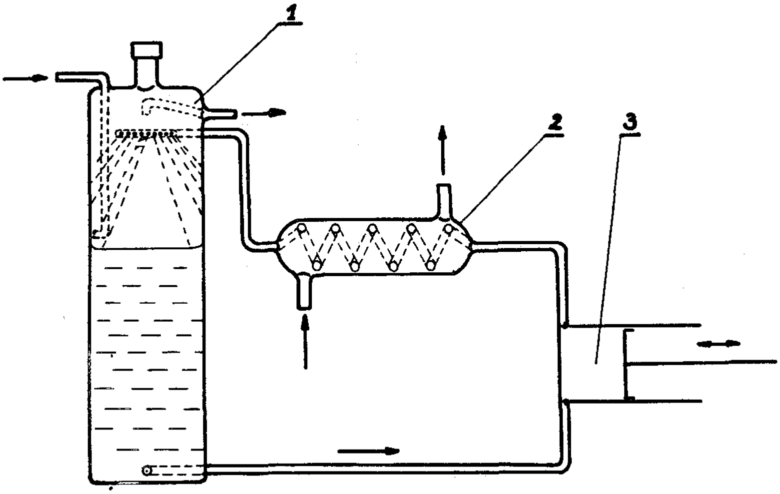

FIGURE 2 Device for isolation of organic compounds from liquid phase. 1—unit for expansion of the liquid phase surface; 2—heat exchanger; 3—syringe pump.

combustion products were washed with an aqueous solution of isopropanol[26] into a coulometric cell, followed by argentometric titration to a preset end-point potential.[27,28] The described unit can be employed for isolation of organic compounds from aqueous samples of various volume in a periodic exhaustive extraction or continuous manner, which is shown schematically in Figure 3.

## Reagents

It was decided to carry out the model investigations with organochlorine compounds which, due to their mutagenic and carcinogenic character, high stability and universal occurrence are one of the most dangerous pollutants. Four compounds differing considerably with respect to boiling point, aqueous solubility and distribution coefficients between the gaseous and liquid phase were selected for the investigations: chloroform (b.p. 61°C), trichloroethylene (b.p. 87°C), chlorobenzene (b.p. 132°C) and dichlorobenzene (b.p. 172.5°C). All compounds (POCh, Gliwice, Poland) were of analytical reagent grade. The concentrations of the stock solutions were checked daily by means of a stripping technique.

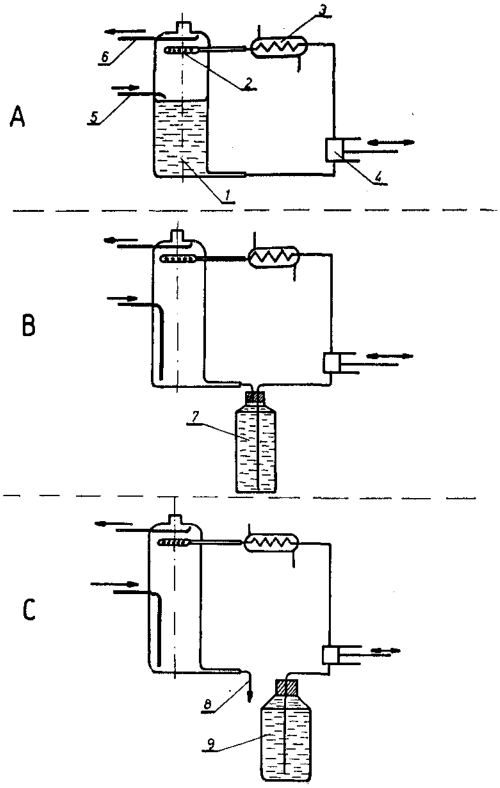

FIGURE 3 Application of the device for isolation of organics from aqueous samples of various volume. A. Periodic method—sample from the unit. 1—unit for expansion of the liquid phase surface; 2—ring with 15 holed jets; 3—heat exchanger; 4—syringe pump; 5—gas inlet; 6—gas outlet. B. Periodic method—sample from an external container. 7—external container with an aqueous sample. C. Continuous method. 8—outlet of water stream from the unit; 9—container with an aqueous sample.

## Procedure

Model investigations of three variants of application of the designed device for expansion of the surface of liquid phase using a spray technique were carried out, depending on the placement and supply of the analyzed solution:

A. Internal periodic system—the investigated solution was placed in a spray vessel and recirculated in a closed system (Figure 3A).

B. External periodic system—the investigated solution was placed in an additional vessel connected in a closed system with a pump and the spray vessel (Figure 3B).

C. Continuous system—the investigated solution was delivered by a pump to the spray vessel in a continuous mode without returning the spent solution (Figure 3C).

In all variants there was a possibility of varying the flow rate of the analyzed solution ($V_s$), the flow rate of air ($V_g$) and the temperature ($t$) of the heat exchanger heating the delivered solution (2 in Figure 2).

When investigating periodic systems of isolation of organics from the analyzed model solution (Figures 3A and 3B) the determinations of VOÇl were carried out at maximum attainable flow rate of the solution ($V_s = 250\,\mathrm{cm}^3/\mathrm{min}$; the decisive factor was the output of a piston pump)—hence, the analyzed sample passed repeatedly through the device for expansion of the surface of liquid phase until isolation of the organochlorine compounds was achieved—and at maximum flow rate of purified air through the unit equal to $250\,\mathrm{cm}^3/\mathrm{min}$, which still ensured complete combustion of the liberated compounds.

In the course of investigations a variable parameter was temperature of the solution delivered to the unit. Model solutions were heated in the heat exchanger to temperatures ranging from 25 to 60°C in the case of system A and from 25 to 90°C in the case of system B. On the other hand, in the case of third system for isolation of organic compounds from aqueous samples (system C) the effect of flow rate of the analyzed aqueous solution ($30$–$250\,\mathrm{cm}^3/\mathrm{min}$) and flow rate of gas through the unit ($50$–$270\,\mathrm{cm}^3/\mathrm{min}$) on the recovery $R$ (%) of organochlorine compounds from model aqueous solutions was studied at constant temperature of the solution delivered from the heat exchanger to the device for expansion of the surface of liquid phase using a spray technique.

## RESULTS AND DISCUSSION

A. Internal periodic system (Figure 3A). The effect of temperature on the recovery of $CHCl_3$ from model solutions in distilled water is shown in Figure 4. For temperature of the analyzed sample on the order of 50°C the time of attaining complete recovery of chloroform does not exceed 20 min. For the same temperature, the dynamics of recovery of the remaining three organochlorine compounds from model solutions was also studied. The obtained results are shown in the next figure. It follows from Figure 5 that after 30 min the recovery of these compounds reaches the value on the order of 94–100%. Statistical analysis of the degree of recovery of the investigated organic compounds from the aqueous phase was performed on the basis of 7 parallel determinations for each of the four organic compounds. The results are listed in Table I. The developed method is characterized by high precision of determinations ($t_{95;7} \cdot \bar{s} < 3\%$).

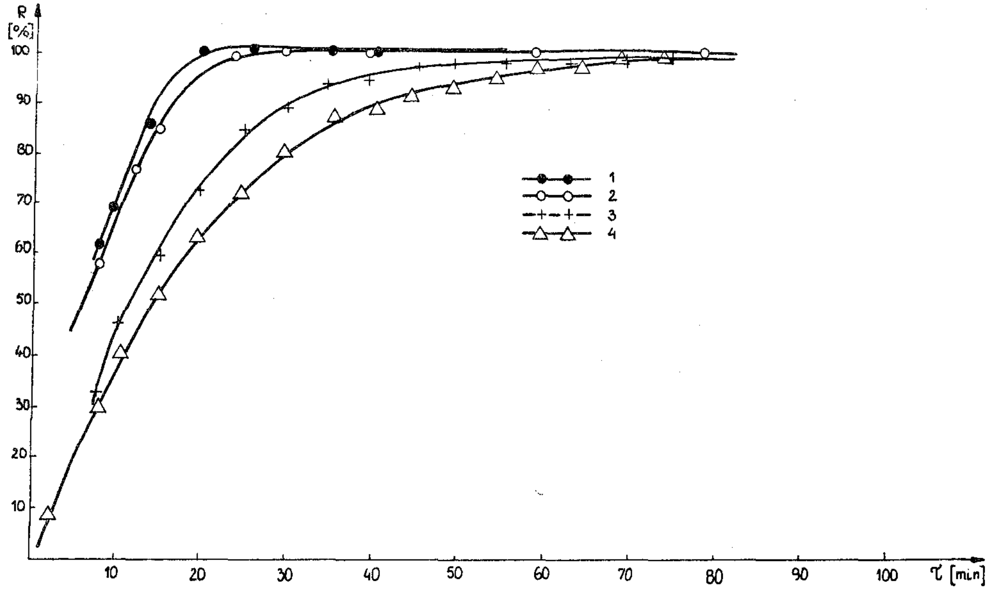

FIGURE 4 The effect of solution temperature on the rate of VOCl recovery from model solutions of $CHCl_3$ using an internal periodic system ($V_g = 250\,cm^3/min$; $V_s = 250\,cm^3/min$; $V_L = 0.4\,dm^3$; $c_{VOCl} = 0.3$ ppm by weight). 1—$t = 50°C$. 2—$t = 60°C$. 3—$t = 35°C$. 4—$t = 25°C$.

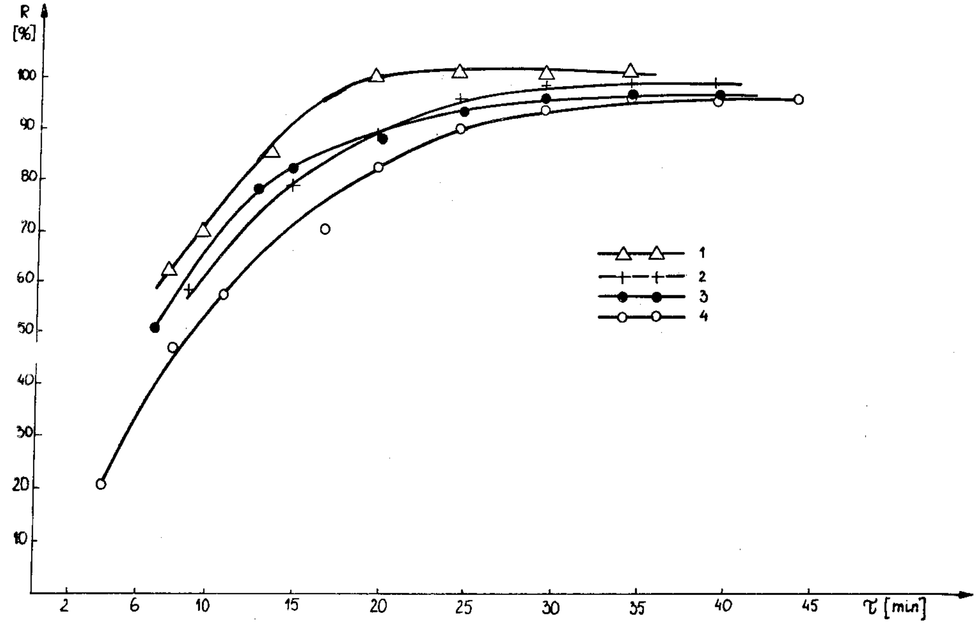

FIGURE 5 The dynamics of VOCl recovery from model solutions of volatile organics using an internal periodic system ($t=50°C$; $V_g=250\,cm^3/min$; $V_s=250\,cm^3/min$; $V_L=0.4\,dm^3$; $c_{VOCl}=0.13 \div 0.30$ ppm by weight). 1—chloroform. 2—chlorobenzene. 3—trichloroethylene. 4—dichlorobenzene.

TABLE I

The recovery of VOCl from model solutions of volatile organics using a periodic internal system of analysis ($t=50°C$, $V_g=250\,cm^3/min$, $V_s=250\,cm^3/min$, $c_{VOCl}=0.13 \div 0.50$ ppm by weight).

| Compound | b.p. (°C) | $n$ | $\bar{R}$ (%) | $s_R$ | $t_{(95;7)} \cdot \bar{s}$ |
|---|---|---|---|---|---|
| Chloroform | 61 | 7 | 98.2 | 2.57 | 2.38 |
| Trichloroethylene | 87 | 7 | 95.2 | 3.17 | 2.93 |
| Chlorobenzene | 132 | 7 | 98.7 | 3.19 | 2.95 |
| Dichlorobenzene | 172.5 | 7 | 97.3 | 3.22 | 2.98 |

B. External periodic system. Analogously to the former system, the investigations of the dynamics of VOCl recovery were carried out as a function of temperature of the solution delivered to the unit for expansion of the surface of liquid phase using a spray technique. It follows from the experimental data shown in Figure 6 that only an elevation of the solution temperature to 90°C ensures reaching the degree of recovery ranging from 95 to 100% in 30–40 min. The dynamics of recovery of all four compounds used in model investigations was checked at this

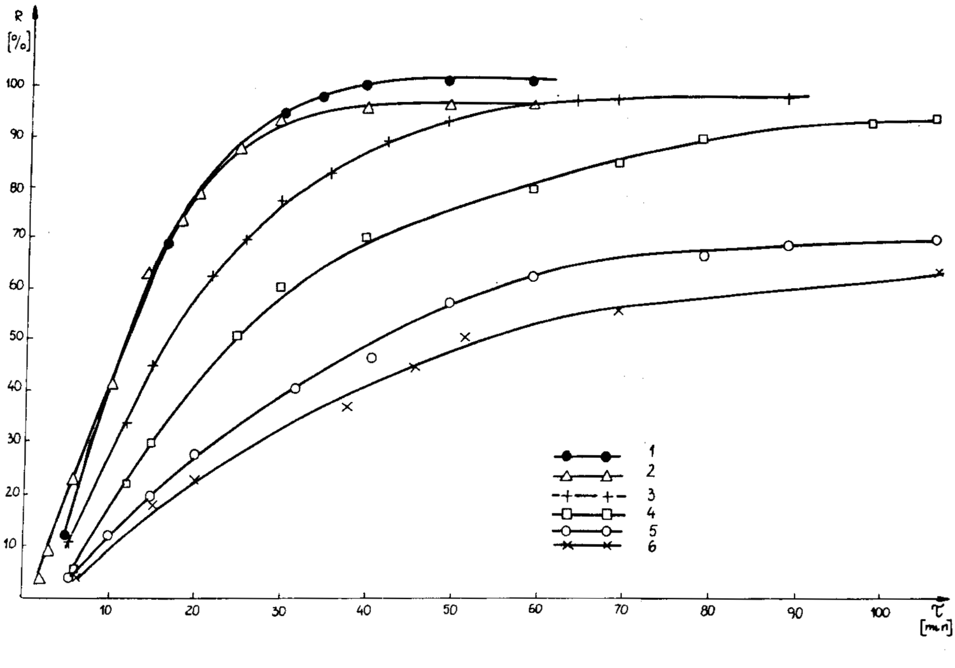

FIGURE 6 The effect of solution temperature on the rate of VOCl recovery from model solutions of $CHCl_3$ and $C_6H_5Cl$ using an external periodic system ($V_g = 250\,cm^3/min$; $V_s = 250\,cm^3/min$; $V_L = 1\,dm^3$; $c_{VOCl} = 0.06 \div 0.25\,ppm$). 1—$CHCl_3$; $t = 90°C$. 2—$C_6H_5Cl$; $t = 90°C$. 3—$CHCl_3$; $t = 60°C$. 4—$C_6H_5Cl$; $t = 60°C$. 5—$CHCl_3$; $t = 25°C$. 6—$C_6H_5Cl$; $t = 25°C$.

temperature, which is presented in Figure 7. The studies confirmed the possibility of attaining the recovery on the order of 92–98% for all compounds already after 30 min. Statistical analysis of the recovery was carried out also for this system by performing 7 parallel VOCl determinations for each of organochlorine compounds isolated from the model solutions and their mixture in artificial sea water.[29] The results of statistical evalution are compiled in Table II. The lack of background in the case of degassed sea water (and hence the matrix with volatile organic compounds removed), in the case of 10% aqueous solution of NaCl and in the case of artificial sea water indicates the lack of influence of inorganic chlorides present in the matrix on the results of determinations.

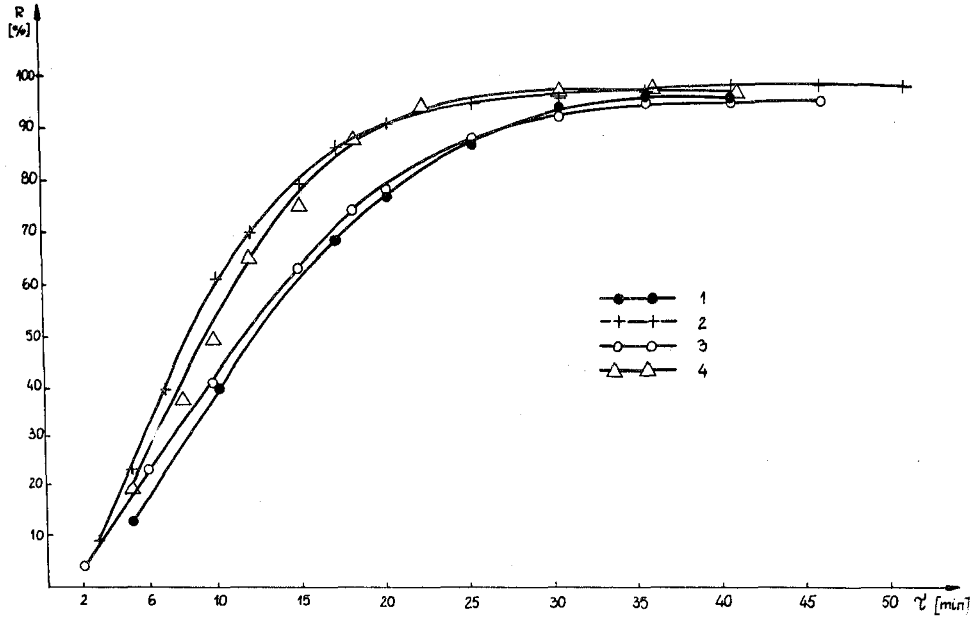

FIGURE 7 The dynamics of VOCl recovery from model solutions of volatile organics using an external periodic system ($t = 90°C$; $V_s = 250\,cm^3/min$; $V_g = 250\,cm^3 min$; $V_L = 1\,dm^3$; $c = 0.06 \div 0.25$ ppm VOCl by weight). 1—chloroform. 2—trichloroethylene. 3—chlorobenzene. 4—dichlorobenzene.

TABLE II

The recovery of VOCl from model solutions of volatile organics using a periodic external system of analysis ($t=90°C$, $V_g=250\,cm^3/min$, $V_s=250\,cm^3/min$, $c_{VOCl}=0.06\div 0.25$ ppm by weight).

| Compound | $n$ | $\bar{R}$ (%) | $s_R$ | $t_{(97;7)}\cdot\bar{s}$ |
|---|---|---|---|---|
| Distilled water | 2 | 0 | | |
| Degassed sea water | 2 | 0 | | |
| 10% NaCl solution | 2 | 0 | | |
| Artificial sea water | 2 | 0 | | |
| Chloroform | 7 | 97.2 | 2.70 | 2.10 |
| Trichloroethylene | 7 | 95.5 | 3.85 | 3.56 |
| Chlorobenzene | 7 | 94.3 | 3.50 | 3.24 |
| Dichlorobenzene | 7 | 96.1 | 4.01 | 3.71 |
| Mixture of four compounds in artificial sea water | | | | |
| $c_{VOCl}$: ~0.25 ppm | 7 | 97.4 | 3.28 | 3.03 |
| $c_{VOCl}$: ~0.08 ppm | 7 | 96.2 | 2.43 | 2.25 |

C. Continuous system. After carrying out preliminary investigations it was decided to perform the process of liberation of organic compounds from the aqueous phase after heating it to 90°C. The effect of flow rate of air through the unit for surface expansion and flow rate of the liquid phase delivered to this unit on the VOCl recovery from the model aqueous solutions of chloroform was studied. The obtained dependences are shown in the form of respective plots in Figures 8 and 9. As follows from Figure 8, in the case of a continuous system for isolation of organic compounds from the aqueous phase according to Figure 3C the decisive effect on the VOCl recovery has the rate of delivery of solution by a piston pump. This is probably associated with the thickness of layer dropping down the wall of the unit for expansion of the surface of liquid phase and with the dynamics of transfer of compounds from the liquid to gaseous phase. At the rates of delivery of the liquid phase lower than $60\,cm^3/min$ the recovery reaches the level of 72–75% for the analyzed samples of volume $V_L \cong 500\,cm^3$. No significant effect of the air flow rate on the VOCl recovery was observed (Figure 9). Further investigations of the continuous system were carried out at the flow rate of air $V_g=250\,cm^3/min$ and the rate of delivery of the liquid phase $V_s=45\,cm^3/min$. The results of

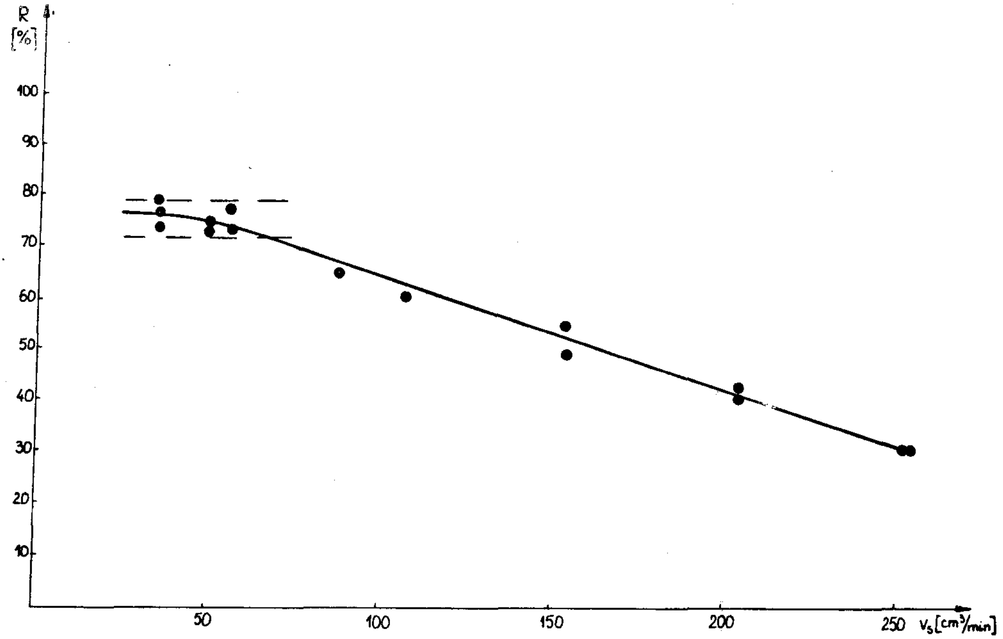

FIGURE 8 The effect of flow rate of the investigated solution on the recovery ($R$) of VOCl from model solutions of $CHCl_3$ using a continuous system ($t=90°C$; $V_g=250\,cm^3/min$; $V_L=500\,cm^3$; $c_{VOCl}=0.16\div0.25$ ppm by weight).

statistical analysis are presented in Table III. In the case of application of the continuous system for isolation of organochlorine compounds from model aqueous solutions the obtained VOCl recovery did not reach 100%; however, the recovery for all 4 investigated compounds (of substantially different volatility) is of the same order ($\bar{R}=74\pm2\%$) with simultaneous high precision of determinations. This permits to utilize also the continuous system for isolation of organic compounds from the aqueous phase after introduction of the respective empirical coefficient which, e.g., for $\bar{R}=74\%$ is equal to $f=1.3514$. It should be pointed out that analogous results (from statistical point of view) were also obtained in the case of determination of VOCl for 4 organic compounds present in a model mixture, i.e. in artificial sea water.[29] The total VOCl concentration was $c_{VOCl}=7.4\div13.1$ ppb.

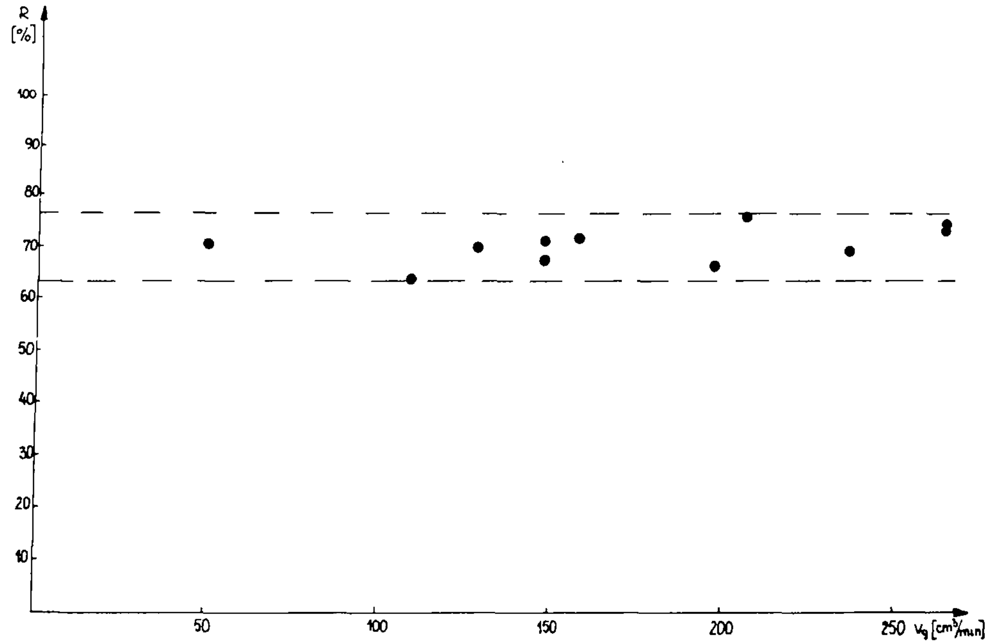

FIGURE 9 The effect of flow rate of air on the VOCl recovery from model solutions of $CHCl_3$ ($t = 90°C$; $V_s = 45\,cm^3/min$; $V_L = 500\,cm^3$; $c_{VOCl} = 0.20 \div 0.23$ ppm by weight).

TABLE III

The recovery of VOCl from model solutions of volatile organics using a continuous system ($t \simeq 90°C$, $V_g = 250\,cm^3/min$, $V_s = 45\,cm^3/min$, $V_L \cong 500\,cm^3$, $c_{VOCl} = 0.2 \div 0.4$ ppm by weight).

| Compound | $n$ | $\bar{R}$ (%) | $s_R$ | $t_{(95;7)} \cdot \bar{s}$ |
|---|---|---|---|---|
| Chloroform | 7 | 72.0 | 1.34 | 1.24 |
| Trichloroethylene | 7 | 75.8 | 3.77 | 3.49 |
| Chlorobenzene | 7 | 73.1 | 2.06 | 1.91 |
| Dichlorobenzene | 7 | 73.7 | 3.25 | 3.01 |
| Mixture of four compounds in artificial sea water ($c_{VOCl} = 7.4 \div 13.3$ ppb, $V_L = 6\,dm^3$) | 7 | 74.1 | 3.00 | 2.77 |

## GENERAL CONCLUSIONS

The developed simple apparatus for isolation of organic compounds from the aqueous phase can be successfully used in three variant designs. Their practical application will depend primarily on the size of an aqueous sample to be analyzed, the increase in the volume of the sample (in the case of periodic systems) naturally resulting in prolonging the time necessary for isolation of compounds from the aqueous phase and, hence, the time of analysis. It is highly probable that the use of a piston pump of higher output for delivery of the liquid phase would enable further shortening of the analysis time by increasing the number of cycles: sample delivery—spraying in the unit for expansion of the surface of liquid phase until the moment of attaining possibly high degree of isolation of organic compounds from an aqueous sample.

The continuous system enables analysis of water samples unlimited by the volume of a unit or an external vessel. Although in this case the recovery of the order of 100% is not reached, but since this parameter is to a large extent independent of the boiling point and solubility of organic compounds in water, it is possible to introduce a suitable correction coefficient. The detection limits of methods utilizing the proposed device for isolation of organic compounds from the liquid phase will significantly depend on the used method of final determination. In the case of coulometric determination of chlorides formed in the process of oxidative mineralization of organochlorine compounds in the gaseous phase it is possible to determine with good precision the concentrations of the order of 7.4 ppb of VOCl by weight. The continuous system of isolation of organic compounds can also be employed for monitoring organic pollutants of water in an on-line mode. No effect of inorganic ions and chlorides in particular on the VOCl recovery was observed both for aqueous NaCl solutions and artificial sea water.

In the case of all three described designs of the device the use of the Purge and Trap technique is possible, which would facilitate employment of gas chromatography for the determination of organic compounds isolated from the aqueous matrix. Utilization of sorbent of low affinity for water (e.g. Tenax GC or other porous polymers) would eliminate the problem of water vapour, which is also present in a stream of gas at the outlet of the unit for expansion of the surface of liquid phase and, at the same time, would significantly improve the detection limit.

## Acknowledgements

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