THEORY OF THE EQUILIBRIUM IN A MICROAPPARATUS FOR THE ISOLATION AND CONCENTRATION OF ORGANIC SUBSTANCES FROM WATER BY CONTINUOUS STEAM DISTILLATION-EXTRACTION*

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The phase equilibrium establishing in a microapparatus designed for the isolation and concentration of organic substances from water by continuous steam distillation-extraction is treated. This technique, used for the preconcentration of water pollutants followed by the gas chromatographic analysis of the extract, is suitable for organic substances with boiling temperatures higher than that of water which form azeotropic mixtures with water, the boiling temperatures of which are lower than those of water and the organic substances themselves. The organic solvent used for the extraction must have a very low boiling temperature. The recovery from the whole procedure and the concentration factor depend on the volumes of the water sample and the organic solvent as well as on the volume of the space where the extraction of the organic substance from the aqueous condensate takes place.

The relatively new preconcentration technique of continuous steam distillation-extraction[1,2] is finding increasing use in the trace analysis of waters. This technique supplements conveniently other enrichment techniques such as the isolation of substances from water sample with an inert gas stream[3,4], with a liquid, or with a sorbent[5], or the various modifications of distillation methods[6]. It is an advantage of this new approach that, in addition to nonpolar substances, relatively nonvolatile and polar substances can also be isolated, which is often impossible with the conventional methods. The steam distillation-extraction procedure is simple, rapid, and straightforward, and the extract obtained is amenable to gas chromatographic analysis without any additional concentration or purification.

The aim of the present work was to characterize the types of organic substances for which the continuous steam distillation-extraction approach is suitable as a preconcentration step for their gas chromatographic analysis.

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APPARATUS FOR CONTINUOUS STEAM DISTILLATION-EXTRACTION

The layout of the apparatus is shown in Fig. 1. Water vapour from the sample, enriched with the organic substances, distills from flask **3** and the distillate condenses in the central part of the apparatus. Simultaneously, a suitable low-boiling organic solvent distills from flask **4** and also condenses in the central part. In this manner the organic substances from the aqueous condensate are extracted into the organic solvent in the central part of the apparatus. The two liquid phases, which separate on the bottom of the central part, return through their overflow arms **1** and **2** to their flasks. The water sample loses the organic substances while the organic solvent in flask **4** becomes enriched with them. The solvent coming to the central part is virtually pure, or, strictly speaking, very low contaminated by the isolated substances in amounts corresponding to their vapour pressure above the solvent in flask **4**. The process is conducted until the equilibrium is reached, which typically takes 1 to 1·5 hours[1,2].

Description of the Equilibrium

For very low concentrations, the mole fractions of solute in the various parts of the apparatus can be written as

$$x_1 = D_c \left(\mathscr{V}_{org} / \mathscr{V}_{aq} \right) x_2 \qquad (1)$$

$$y_2 = K_{aq} x_3 \qquad (2)$$

$$y_4 = K_{org} x_4 . \qquad (3)$$

In equilibrium, where $x_2 = y_3$ and $x_1 = y_4$, Eqs $(1)-(3)$ give

$$x_4 = D_c \left(K_{aq} / K_{org} \right) \left(\mathscr{V}_{org} / \mathscr{V}_{aq} \right) x_3 . \qquad (4)$$
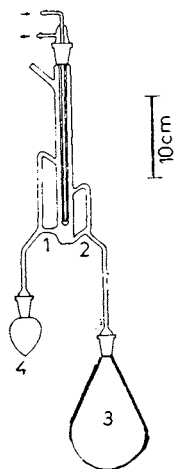

Fig. 1

All-glass microapparatus for the steam distillation-extraction. Description in the text

Assuming that the amount of solute in the gaseous phase is negligibly low as compared to its amount in the liquid phases, and that the average molar volumes of the water sample in flask 3 and of the aqueous phase in the central part 2 are identical, and the same for the organic phase in flask 4 and in the central part 1, we have

$$x_1 = (m_1/M)(\mathscr{V}_{org}/V_1) \tag{5}$$

$$x_2 = (m_2/M)(\mathscr{V}_{aq}/V_2) \tag{6}$$

$$x_3 = (m_3/M)(\mathscr{V}_{aq}/V_3) \tag{7}$$

$$x_4 = (m_4/M)(\mathscr{V}_{org}/V_4). \tag{8}$$

Combining Eqs (4), (7), and (8), the mass balance of solute over the entire system is obtained as

$$m_4/V_4 = D_c(K_{aq}/K_{org})(m - m_1 - m_2 - m_4)/V_3. \tag{9}$$

Since Eqs (2) and (6), or (3) and (5), are equivalent in the equilibrium, combination with Eq. (8), or Eq. (1), gives

$$m_1 = K_{org}(V_1/V_4) m_4 \tag{10}$$

$$m_2 = (K_{org}/D_c)(V_2/V_4) m_4. \tag{11}$$

The recovery from the distillation-extraction, defined as the mass ratio of solute in the extract to its initial total amount in the water sample,

$$R = m_4/m \tag{12}$$

and the concentration factor, defined as the ratio of the corresponding concentrations,

$$F = c_4/c_{3(0)} = R(V_3/V_4) \tag{13}$$

are obtained, by means of Eqs (9)−(11), in the forms

$$R = 1/[(1/D_c)(K_{org}/K_{aq})(V_3/V_4) + K_{org}(V_1/V_4) + (K_{org}/D_c)(V_2/V_3) + 1] \tag{14}$$

and

$$F = 1/[(1/D_c)(K_{org}/K_{aq}) + K_{org}(V_1/V_3) + (K_{org}/D_c)(V_2/V_3) + (V_4/V_3)]. \tag{15}$$

Thus R and F depend both on the volumes in the apparatus and on the physico-chemical parameters of the system, described by the D_c, K_{org}, and K_{aq} constants which, in general, depend on the concentration of solute, on the medium, and on the temperatures used. For trace analysis of organic substances in water, the concentration of solute is negligibly low, which simplifies the estimate of the constants.

For very low concentrations and for the ideal behaviour of the gas phase, the distribution constant of solute can be written as

$$K = y_i/x_i = \gamma_i(x_i)\, P_i^0/P_j^0 = \gamma_i(x_i)\, \alpha_{ij} . \tag{16}$$

The activity coefficient can be estimated by means of chemical thermodynamics relations, *e.g.*, the Wohl or Redlich–Kister series, the NRTL equation, *etc.* Let P_j^0 be the pressure of saturated vapours of the substance in which the solute is dissolved, at the given temperature; the vapour pressure at boil attains the value of the pressure inside the apparatus, which is usually atmospheric pressure, and then

$$K = \gamma_i(x_i)\, P_i^0/P_{total} , \tag{17}$$

where P_i^0, the saturated vapour pressure of solute at the boiling temperature of the solution, can be calculated from Antoine's equation. Eqs (16) and (17) serve as the starting relations for estimating the distribution constants K_{aq} and K_{org}.

Constant K_{aq}. This constant is given by Eq. (16) or Eq. (17) if $\gamma_i(x_i)$ is the activity coefficient of solute in water at the temperature occurring in flask **3** (approximately the boiling temperature of water or the modified aqueous solution), which for the majority of limiting concentrations of organic substances in water is much greater than unity, and so its product with the saturated vapour pressure P_i^0 is usually higher than the total pressure. In this manner, K_{aq} attains values greater than unity, as a result of which the gaseous phase, and thus the distillate, becomes richer in the organic substance than the water sample in flask **3**.

The following cases fall in this class: *1*) The boiling temperature of the organic substance is lower than that of water and the organic substance forms no azeotropic mixture with water or it forms an azeotropic mixture with a boiling temperature minimum. *2*) The substance in question has a boiling temperature higher than water and it forms with water an azeotropic mixture with a boiling temperature minimum (the majority of organic substances). Here the distillate becomes enriched with the organic substance only if the composition of the aqueous phase in flask **3** is within the region of azeotrope-pure water. This is practically always the case for waters polluted by trace amounts of contaminants, in concentrations not exceeding $mg\,l^{-1}$ levels.

The unfavourable cases encompass organic substances with boiling temperatures higher than that of water which do not form azeotrope or which form an azeotrope with a boiling temperature maximum. However, these cases are much rarer than those given above.

Constant K_{org}. This constant is also given by Eq. *(16)* or *(17)*. For similar polarities of the organic solute and the organic solvent, which is also an important condition for a high extraction efficiency in the central part of the apparatus, it is reasonable to assume that the activity coefficient of solute will approach unity even at its very low concentrations. If the boiling temperature of the organic solvent is very low, the saturated vapour pressure of the less volatile component is much lower than the atmospheric pressure, as is its product with the activity coefficient. The K_{org} value then will be lower than unity. It appears that with respect to the K_{org} value, steam distillation-extraction is unsuitable for the isolation of low-boiling substances from water samples.

Concentration distribution ratio D_c. The D_c ratio of solute, for the extraction in the central part of the apparatus, is given by its concentration ratio in the organic to the aqueous phases of the extraction system. Its value can also be estimated by means of the activity coefficients. In equilibrium,

$$x_1 \gamma_{org}(x_1) = x_2 \gamma_{aq}(x_2),\qquad(18)$$

and combined with Eq. *(1)*,

$$D_c = \left[\gamma_{aq}(x_2)\,\mathscr{V}_{aq}\right]/\left[\gamma_{org}(x_1)\,\mathscr{V}_{org}\right].\qquad(19)$$

It is clear from this relation that for the extraction of the organic solute from the aqueous distillate in the central part of the apparatus, the polarity of the organic solvent chosen should approach that of the substance extracted. The solution of the latter in the organic solvent then is nearly ideal, which leads to a decrease in $\gamma_{org}(x_1)$ to a value close to unity and to a shift of the distribution ratio D_c to the maximum. For the distillation-extraction, however, the solvent must have a very low boiling temperature, and so the choice of solvents according to their polarity is practically limited to the pentane–dichloromethane–diethyl ether series. Since the density of dichloromethane is higher than that of water, the distillation flasks and the arm gatings in the central part of the apparatus have to be interchanged for this solvent.

The method of continuous steam distillation-extraction has been used in practice for the determination of low concentrations of chlorinated pesticides[1], polychlorinated biphenyls[1], phenols[2], and fatty acids in waters and sludges[7,8]. The detection limits for the pollutants in water are tenths to tens of $\mu g\,l^{-1}$, according to the type of solute and the chromatographic and detection technique used.

LIST OF SYMBOLS

K_{aq}	gas–liquid distribution constant (given by mole fractions) for the organic solute in water sample
K_{org}	gas–liquid distribution constant (given by mole fractions) for the organic solute in the organic solvent
D_c	liquid–liquid concentration distribution ratio (given by mass concentrations) for the organic solute in the central part of the apparatus
x_1	equilibrium mole fraction of the organic solute in the organic solvent in the central part of the apparatus
x_2	equilibrium mole fracion of the organic solute in aqueous solution in the central part of the apparatus
x_3	equilibrium mole fraction of the organic solute in the water sample
x_4	equilibrium mole fraction of the organic solute in the organic solvent in flask **4**
y_3	equilibrium mole fraction of the organic solute in the gas phase above the water sample in flask **3**
y_4	equilibrium mole fraction of the organic solute in the gas phase above the organic solvent in flask **4**
m_1	mass of the organic solute in the organic solvent in the central part of the apparatus
m_2	mass of the organic solute in the aqueous phase in the central part of the apparatus
m_3	mass of the organic solute in the water sample in flask **3**
m_4	mass of the organic solute in the organic solvent in flask **4**
m	initial mass of the organic solute in the water sample
M	relative molecular mass of the organic solute
V_1	volume of the organic solvent in the central part of the apparatus
V_2	volume of the aqueous condensate in the central part of the apparatus
V_3	volume of the water sample in flask **3**
V_4	volume of the organic solvent in flask **4**
R	recovery of the organic solute from the steam distillation-extraction into the organic solvent
F	concentration factor of the steam distillation-extraction procedure
$\mathscr{V}_{aq}$	average molar volume of the water sample and the extracted aqueous phase in the central part of the apparatus
$\mathscr{V}_{org}$	average molar volume of the organic solvent in flask **4** and the organic phase in the central part of the apparatus
x_i	mole fraction of the organic solute in liquid in the i-th section of the apparatus (in general)
y_i	mole fraction of the organic solute in the gas phase in the i-th section of the apparatus (in general)
$\gamma_i(x_i)$	the Raoult activity coefficient of the organic solute for its mole fraction x_i in the i-th section of the apparatus
$\gamma_{aq}(x_2)$	activity coefficient of the organic solute for its mole fraction x_2 in the aqueous solution in the central part of the apparatus
$\gamma_{org}(x_1)$	activity coefficient of the organic solute in the organic solvent for its mole fraction x_1 in the central part of the apparatus
P_i^0	saturated vapour pressure of the organic solute (in pure state) in the i-th section of the apparatus at a given temperature
P_j^0	saturated vapour pressure of pure solvent (water or the organic solvent) at the temperature corresponding to the boiling temperature

$\alpha_{i,j}$ relative volatility
P_{total} total pressure of the gas phase

REFERENCES

1. Godefroot M., Stechele M., Sandra P., Verzele M.: J. High Resol. Chromatogr. Chromatogr. Commun. *5*, 79 (1982).
2. Janda V., Krijt K.: J. Chromatogr. *283*, 309 (1984).
3. Bellar T. A., Lichtenberg J. J.: J. Amer. Water Works Assoc. *66*, 739 (1974).
4. Grob K.: J. Chromatogr. *84*, 255 (1973).
5. Junk G. A., Richard J. J., Greiser M. D., Witiak D., Witiak J. L., Arguello M. D., Vick R., Svec H. J., Fritz J. S., Calder G. V.: J. Chromatogr. *99*, 745 (1974).
6. Peters F. V.: Anal. Chem. *52*, 211 (1980).
7. Janda V., Pehal F., Hrivňák J.: J. High. Resol. Chromatogr. Chromatogr. Commun. *7*, 540 (1984).
8. Janda V.: *Analysis of Organic Pollutants in Water by Continuous Steam Distillation-Extraction and Capillary Gas Chromatography.* 6th Int. Symposium on Capillary Chromatography, Riva del Garda, May 14—16, 1985.

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