Simultaneous Distillation−Extraction: Theoretical Model and Development of a Preparative Unit

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Simultaneous distillation−extraction (SDE) is routinely used by analysts for sample preparation prior to gas chromatography. As the GC profile of the isolated volatiles must be representative of the original sample, the limits of SDE applicability should be known. In this paper, an equation which agrees very well with the experimental rate of pyridine recovery is proposed. Consequently, the influence of various operating parameters can be simulated. In addition, the recovery of a given molecule can be deduced from its relative volatility and water/solvent partition coefficient. A new preparative device was developed on the basis of these observations. It allows the isolation of volatiles from a matrix at atmospheric pressure, or under vacuum, at room temperature. Therefore, the formation of thermal artifacts is reduced. A distillation column was added in the solvent side to limit possible redistillation. Extraction and separation steps were separated, and the extraction efficiency was improved to increase recovery rates.

In flavor and fragrance analytical laboratories, simultaneous distillation−extraction (SDE) is probably the most familiar technique for isolation of volatiles from a complex matrix. Its efficiency has been compared to those of other aroma isolation techniques, such as direct solvent extraction and headspace.[1] The recovered isolates contain nearly all the flavorings present in the starting material without any nonchromatographable components, in contrast to solvent extraction of a lipid-containing food.[2] Because headspace sampling selects only the most volatile molecules, SDE remains a very common method, in spite of several drawbacks mentioned herein.

Since the design was first published 30 years ago,[3] many improvements have been proposed to overcome its main limitations. The size of the device has been reduced,[4] and this microapparatus allows quantitative recovery of the flavorings. The resulting extracts are concentrated enough to be GC-injected without solvent removal.

The generation of artifacts in the sample flask due to the high temperature required for steam distillation has led analysts to work at reduced pressures.[5,6] In a recent paper, we described a microscale device operating under static vacuum. This closed system prevents losses of volatiles, and high recoveries are obtained without thermal degradation of the sample.[7]

Operating conditions have been optimized using either a Simplex experimental design[8] or by adding a salt to the sample flask to reduce water solubility of the organic compounds. Only one paper[9] reports an SDE design optimization based on the theoretical model proposed by Rijks.[10] This model was established on three assumptions: (1) liquid/liquid extraction occurs between liquid films when solvents are condensing on the cold finger, and extraction in the separator is insignificant; (2) the solvent-to-water partition coefficient approaches infinity (quantitative extraction); and (3) the gas-to-solvent partition coefficient is negligible (no redistillation). However, descrepancies between experimental and theoretical curves (e.g., for phenol and *o*-cresol) occur when using Rijks's kinetics.

In spite of its efficiency, no scaling-up of the technique has ever been proposed. Nevertheless, treatment of large quantities is required when the isolated flavor must be further fractionated prior to usual GC or GC/MS analysis (e.g., chemical isolation of the different functional classes, distillation, etc.), when sensory evaluation of the flavor/fragrance must be performed, and to industrially prepare an essential oil when the usual steam distillation methods are not suitable (e.g., no decantation of the essential oil from water due to low yields).

Starting from our experience with vacuum SDE[7] we undertook the development of a preparative system with the following objectives: operating at atmospheric or reduced pressure for recovery of heat-sensitive flavors under mild conditions, working with solvents more or less dense than water, and creating a versatile and modular system. Such characteristics were not found in any system described in the literature. A patent[11] proposes a device for continuous steam distillation−extraction of volatile substances. However, the term "continuous" applies not to sample feeding but to the extraction process that runs while steam distillation is performed.

The present paper reports such a development in four parts: (1) reinvestigation of the theoretical model to understand the key parameters that influence performance, (2) experimental verification of the model using Godefroot's device, (3) kinetic simulations to elucidate the role of each parameter on recovery, and (4)

(1) Leahy, M. M.; Reineccius, G. A. *Analysis of Volatiles*; Walter de Gruyter & Co.: Berlin, 1984; pp 19−47.

(2) Reineccius, G. In *Flavor Measurement*; Ho, C. T., Manley, C. H., Eds.; Marcel Dekker: New York, 1993; pp 61−75.

(3) Likens, S. T.; Nickerson, G. B. *ASBC Proc.* **1964**, 5−13.

(4) Godefroot, M.; Sandra, P.; Verzele, M. *J. Chromatogr.* **1981**, *203*, 325−335.

(5) Picardi, M.; Issenberg, P. *J. Agric. Food Chem.* **1973**, *21*, 959−962.

(6) Seifert, R. M.; King, A. D. *J. Agric. Food Chem.* **1982**, *30*, 686−790.

(7) Maignial, L.; Pibarot, P.; Bonetti, G.; Chaintreau, A.; Marion, J. P. *J. Chromatogr.* **1992**, *606*, 87−94.

(8) Blanch, G. P.; Tabera, J.; Herraiz, M.; Regglero, G. *J. Chromatogr.* **1993**, *628*, 261−268.

(9) Seidel, V.; Lindner, W. *Anal. Chem.* **1993**, *65*, 3677−3683.

(10) Rijks, J.; Curvers, J.; Noy, T.; Cramers, C. *J. Chromatogr.* **1983**, *279*, 395−407.

(11) Hala, S.; Gajduskova, V.; Zukalova, M. Laboratory continuous extraction−distillation apparatus for determination of volatile organic substances. Czech. Pat. 273145, 1991.
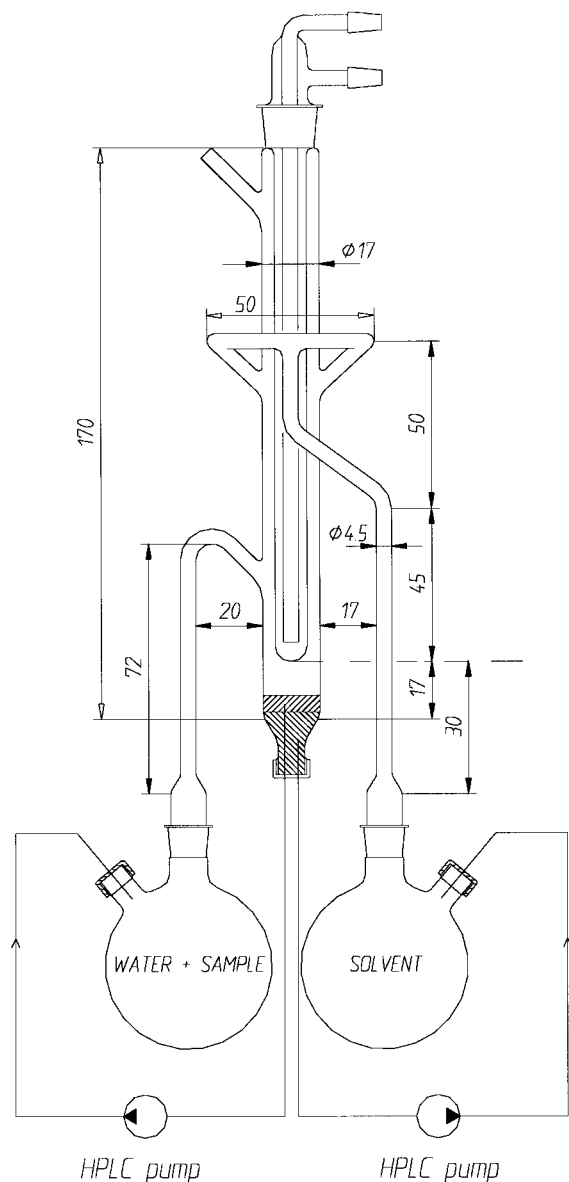
Figure 1. Modified SDE device.

Table 1. Parameters for Vacuum SDE Solvents

	temp (°C)		
	sample	solvent	pressure (mbar)
isooctane	32	18	49
toluene	27	25	37
trichloroethane	28	28	39
trichloroethene	31	9	48

development of a preparative device on the basis of these observations.

EXPERIMENTAL PROCEDURES

SDE Experiments on an Analytical Scale. Godefroot's device was used.[4] In a typical experiment, 200 mL of water and 10 mL of dichloromethane were refluxed in the system. After equilibration of the flows, 509 mg of an aqueous solution of pyridine (7280 mg/L) was introduced into the sample flask through a septum. Recovery kinetics was followed by regularly sampling (250 μL) with a syringe through the septum of the solvent flask. The UV absorbance of the sample was quickly measured, and the sample was immediately reinjected into the solvent flask.

For some measurements, the system was changed according to Figure 1. Liquid flows were determined by pumping the liquids back to the boilers with two HPLC pumps (LC pump 414, Kontron, Zürich, Switzerland). When the flows reached equilibrium, their values were read on the pump displays. The same heating and stirring conditions were carefully reproduced when running the kinetics in the normal device.

The model in Figure 1 was used for relative volatility measurements in water and the solvent. One percent of a 7.30 mg/L aqueous solution of pyridine was distilled, and the UV absorbances in the distillate and in the remaining solution were measured. This experiment was repeated using a 28.8 mg/L pyridine solution in dichloromethane.

The dynamic liquid/liquid partition coefficient was calculated from the absorbances of the two phases collected in the model shown in Figure 1, from a 7.28 mg/L aqueous pyridine solution after equilibration of the liquid flows. These values were confirmed by duplication of this experiment in the normal device and collection of the phases from the separator.

Preparative SDE (Figure 6). (Note: "isooctane" corresponds to 2,2,4-trimethylpentane). *Solvent-to-Water Partition Coefficients.* Dynamic liquid/liquid partition coefficients were determined in the preparative SDE itself. One liter of an aqueous solution of flavoring (40−1000 mg/L) was simultaneously distilled with the solvent. The steam condenser was connected to a flask instead of to the separator. Phases collected in this flask were separated without further stirring, and their flavoring concentrations were quantified by HPLC or UV spectrophotometry.

Gas-to-Solution Partition Coefficients. Dynamic air-to-solution partition coefficients were determined in the preparative SDE to take into account the influence of the device. One liter of an aqueous solution of a flavoring or 100 mL of the solvent solution was distilled and condensed in the steam or in the solvent condenser, respectively. Concentration of the first condensate fraction was quantified by UV spectrophotometry.

Experiments at Atmospheric Pressure. About 2700 mL of sample solution and 50 mL of solvent (100 mL for kinetic experiments) were used. Both flasks were maintained at boiling temperatures and magnetically stirred. The phase separator and condensers were refrigerated at −1 °C.

For kinetic experiments, only one volatile was present in the sample flask, and its recovery was followed in the solvent flask by periodically collecting 0.150 mL of the solution with a syringe and measuring its UV absorption. This sample amount was reinjected into the solvent flask immediately after measurement.

Experiments under Vacuum. Experimental conditions were the same as those for atmospheric batches. Temperatures of the sample and solvent flasks, as well as internal pressure, were carefully regulated according to Table 1.

UV Measurements. Absorbances were measured in a 1 cm quartz cell at 257, 276, 275, 258, 285, and 269 nm for pyridine, vanillin, coumarin, 2-phenylethanol, 2,5-dimethyl-4-hydroxy-3(2H)-furanone (2,5-DHF), and 2-propanone, respectively, using a Uvikon 725 UV spectrophotometer (Kontron). During the kinetic experiment with pyridine and coumarin, 1 mm cells were used to minimize the volume collected and to avoid further dilution of the sample.
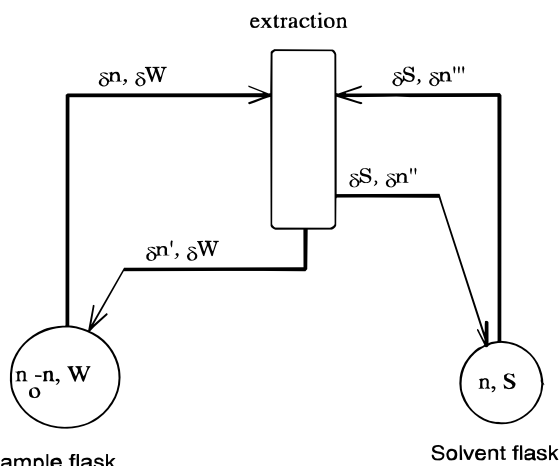
Figure 2. Flowsheet of SDE.

Curve-Fitting. The parametric equations were adjusted to the experimental data using the curve-fitting TableCurve 2D for Windows software (Jandel Scientific, Erkrath, Germany).

HPLC. Two Model 6000 pumps (Waters, Milford, MA) and a Micro UVVIS20 detector (Carlo Erba, Milan, Italy) were monitored by a PC workstation equipped with a MAXIMA 820-33 software (Waters). Fifteen milliliters of solution was injected onto a reversed phase column (Bio-Sil C18, 150 mm × 4.6 mm, particle size 5 mm, Bio-Rad, Richmond, CA). The mobile phase was a 20/80 mixture of acetonitrile and pH 7.0 phosphate buffer at a flow rate of 2 mL/min. Detection was performed at 265 nm.

DISCUSSION

Theoretical Model on an Analytical Scale. When operating with the analytical vacuum SDE, a fine emulsion was observed in the upper phase of the separator, suggesting that extraction took place there. Therefore, Rijks's model was reconsidered without the previously mentioned assumptions.

When operating for a single molecule, SDE flows can be represented as shown in Figure 2. An amount of the flavoring (dn) is codistilled with water (dW), and the condensed aqueous solution is continuously extracted by the distilled solvent (dS), which can, itself, contain a small amount of the flavoring (dn'''). Water returns to the boiler with the remaining volatile (dn'), whereas the solvent returns to its flask with the extracted flavoring (dn'').The extraction is regulated by the partition coefficient,

$$K = \frac{C_{solvent}}{C_{water}} \tag{1}$$

Assuming that the extraction equilibrium is reached,

$$K = \frac{\delta n'' \delta W}{\delta S \, \delta n'} \tag{2}$$

that the flavoring does not accumulate in the extractor,

$$\delta n - \delta n' = \delta n'' - \delta n''' \tag{3}$$

and that the volatile concentration in the vapor phase is proportional to that in the liquid phase,

$$\frac{\delta n''}{\delta S} = k_s \frac{n}{S} \tag{4}$$

gives, from (3) and (4),

$$\delta n' = \delta n + k_s \frac{n}{S} \delta S - \delta n'' \tag{5}$$

Then, (4) becomes

$$\frac{\delta n'}{\delta W} = \frac{\delta n''}{K\delta S} = \frac{\delta n' + \delta n''}{\delta W + K\delta S} \tag{6}$$

Combining (5) and (6) gives

$$\delta n' = \frac{\delta n + k_s \frac{n}{S} \delta S}{\delta W + K\delta S} \delta W \tag{7}$$

Assuming the concentration of flavorings in the steam to be proportional to that in the aqueous phase (the water quantity W being constant in the sample flask),

$$\frac{\delta n}{\delta W} = k_w \frac{n_o - n}{W} \tag{8}$$

Combining (7) and (8) gives

$$\delta n' = \frac{\delta W k_w (n_o - n) S + k_s W n \delta S}{WS(\delta W + K\delta S)} \delta W \tag{9}$$

Then the amount of flavoring arriving in the sample flask is given by

$$dn = \delta n - \delta n' \tag{10}$$

or, using (8) and (9),

$$dn = \frac{n - n_o}{W} k_w \delta W - \frac{\delta W k_w (n_o - n) S + k_s W n \delta S}{WS(\delta W + K\delta S)} \delta W \tag{11}$$

$$= \frac{k_w SKn_o - (k_w SK + k_s W) n}{WS(\delta W + K\delta S)} \delta W \delta S \tag{12}$$

If the distillation flows F_s and F_w are considered to be constant,

$$\delta_s = F_s \, dt$$

$$\delta_w = F_w \, dt$$

Substituting these into (12) gives

$$dn = \frac{k_w SKn_o - (k_w SK + k_s W) n}{WS(F_w + KF_s)} F_w F_s \, dt \tag{13}$$

(13) can be written as

$$dn = (\alpha n_o - \beta n) \, dt \tag{14}$$

Table 2. Symbols Used

symbol	definition
n_o	initial mass of volatile in the sample flask
n	mass of volatile in the solvent flask
δn	mass of volatile codistilled with water
$\delta n'$	mass of flavoring returning to the sample flask
$\delta n''$	mass of flavoring extracted by the solvent
$\delta n'''$	mass of flavoring codistilled with the solvent
k_w	air-to-water partition coefficient[a]
k_s	air-to-solvent partition coefficient[a]
K	solvent/water partition coefficient
W	volume of water
δW	volume of distilled water
S	volume of solvent
δS	volume of distilled solvent

[a] For measurement convenience, k_w and k_s are expressed as a ratio of the concentration (mg/L) of the *condensed* vapors to that of the solution.

Table 3. Operating Parameters of the Analytical SDE for Pyridine Recovery

parameter	F_s (mL/min)	F_w (mL/min)	K^a	K^b	k_s	k_w
value	1.3 ± 0.1	0.85 ± 0.05	11.5	3.3	0.02	20.5

[a] Coefficient at equilibrium. [b] Dynamic coefficient measured with the concentrations of the liquids in the separator.

After integration, (14) becomes

$$-\ln\left(\frac{\alpha}{\beta}n_o - n\right) = \beta t + C \tag{15}$$

Since $n = 0$ when $t = 0$,

$$\ln\left(\frac{\alpha n_o}{\alpha n_o - \beta n}\right) = \beta t \tag{16}$$

or

$$n = \frac{\alpha}{\beta}n_o(1 - e^{-\beta t}) \tag{17}$$

The total amount extracted is then given by the equation

$$n = n_o\frac{k_w SK}{k_w SK + k_s W}[1 - e^{-[(k_w SK + k_s W)F_s F_w t/WS(F_w + KF_s)]}] \tag{18}$$

When the relative volatility of the volatile in the solvent is negligible ($k_s \approx 0$), the equation can be simplified:

$$n = n_o[1 - e^{-[k_w KF_s F_w t/W(F_w + KF_s)]}] \tag{19}$$

Validation of the Model on an Analytical Scale. To verify the equation, various parameters (F_s, F_s, K, k_w, k_s) were measured (Table 3), and a kinetic experiment was run using pyridine as substrate.

Air-to-water partition coefficients were directly evaluated in the analytical SDE to take into account the device's influence. Since the composition of the vapor is proportional to that of the liquid phase,

$$\frac{dn}{dW} = k\frac{n_o - n}{W_o - W} \tag{20}$$

Integration of this equation gives the relative volatility:

$$k = \frac{\ln(1 - n/n_o)}{\ln(1 - W/W_o)} \tag{21}$$

Two percent of the starting aqueous or dichloromethane solution of pyridine was distilled, and the concentration of the condensate was used to calculate k at the distillation temperature. Pyridine appeared to be quickly steam distilled, whereas its redistillation from dichloromethane was very low (Table 3).

The liquid/liquid partition coefficient of pyridine was determined at equilibrium by vigorously stirring both phases. However, this value ($K = 11.5$) did not lead to a curve shape in agreement with the experimental data. Its value was then measured again using the concentrations of the phases sampled in the SDE separator at the beginning of an experiment. This dynamic value appeared to be dramatically lower ($K = 3.3$), indicating a poor extraction efficiency of the system under normal working conditions.

Equation 18 was used as a parametric curve in which K (dynamic), k_s, and k_w were replaced by their values and F_s and F_w were allowed to vary:

$$\frac{n}{n_o} = 1 - e^{-0.340 F_s F_w t/(F_w + 3.3 F_s)} \tag{22}$$

To reach operating conditions as soon as possible during the kinetic experiments, the flasks were filled with pure water and solvent and distilled until an equilibrium was reached. A small portion (500 mL) of the stock solution was then injected into the water flask through the septum. The syringe was accurately weighed before and after injection. Taking into account an induction period of 1.35 min, determined graphically, during which no pyridine was present in the solvent flask, all times were shifted by this value. Equation 22 was then compared with the experimental pyridine concentration as a function of time, using a curve-fitting program. A high coefficient of determination was observed ($r^2 = 0.998$) for $F_s = 0.81$ mL/min and $F_w = 1.4$ mL/min, indicating a very good correlation between the model and the experimental results (Figure 3). All residuals were less than 8.5%.

Simulation of SDE Kinetics. For isolation of volatiles prior to GC quantification, the flavoring recovery must be as high as possible. Starting from (18), it was possible to simulate the behavior of a given molecule if its physical constants were known. This was undertaken for compounds which are known to have poor SDE recoveries[12] (Table 4 and Figure 4).

These components illustrated several cases. 2-Propanone steam distills and extracts well but is partially redistilled with the solvent due to its low boiling point. Therefore, it was recovered in less than 1 h, but its curve indicated a yield limited to 97%. No redistillation was observed for the other compounds.

(12) Bartsch, A.; Hammerschmidt, F. J. *Perfumer Flavorist* **1993**, *5/6*, 41−48.
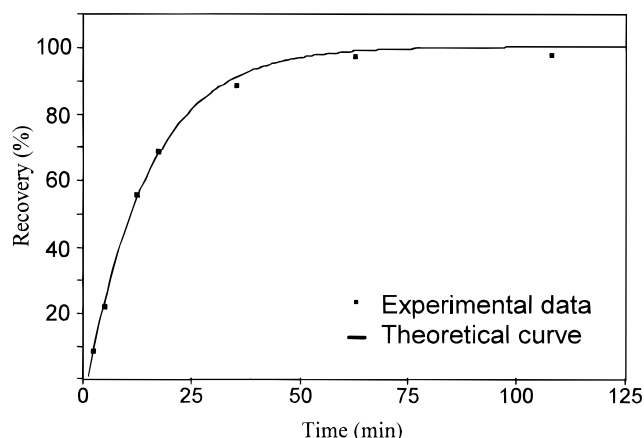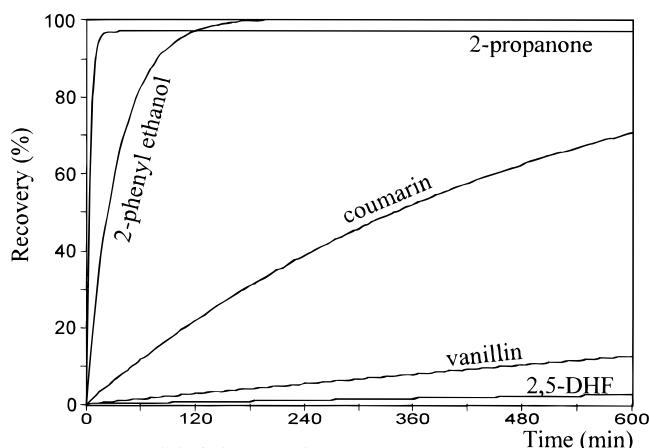
Figure 3. Recovery of pyridine as a function of SDE time.

Table 4. Constants of Some Flavorings

	k_v	K (equilibrium)	K (dynamic)	k_s
2,5-DHF[a]	3.0×10^{-2}	0.67	0.32	$<10^{-2}$
vanillin	2.9×10^{-2}	28	1.8	$<10^{-3}$
2-propanone	59	5.0	2.8	0.29
2-phenylethanol	4.0	23	1.7	$<10^{-3}$
coumarin	0.34	>150	1.4	$<10^{-3}$

[a] 2,5-DHF = 2,5-dimethyl-4-hydroxy-3(2H)furanone.

(2,5-DHF = 2,5-dimethyl-4-hydroxy-3(2H)furanone)

Figure 4. Simulated SDE recovery curves of various molecules.

Vanillin and 2,5-DHF exhibit very low volatilities, and 2,5-DHF is poorly extracted with dichloromethane. SDE appears unsuitable for their isolation. Coumarin and 2-phenylethanol have intermediate volatilities. They could be partially isolated after 1−2 h.

As already mentioned for pyridine, liquid/liquid partition coefficients were determined in two ways. All dynamic values appeared much lower than the static ones. Consequently, the solvent extraction efficiency of an SDE apparatus is critical to the isolation rate, as expected.

Starting from an arbitrary set of values, $k_w = 5$, $K = 2$, $F_s = 1.3$, and $F_w = 0.85$, the influences of the main parameters were simulated in the experimental conditions by varying them separately, as shown in Figure 5. Relative volatilities in water (Figure 5A), which were constant for a given molecule, had the greatest influence. A low liquid/liquid partition coefficient altered the yield; on the other hand, a value higher than 5 did not seem to make a significant improvement (Figure 5B). Increasing the steam and the solvent vapor flows also improved the recovery rate (Figure

5C,D). However, due to the microscale SDE's geometry, these flows were limited by the size of the distillation arms.

All these simulations suggest that Rijks's assumptions could be unsatisfactory: our model is in agreement with an extraction occurring in the separator. Extraction is, by far, not quantitative and is much less efficient in the dynamic mode than expected from measurements at equilibrium. In addition, redistillation occurs with the most volatile compounds.

Development of the Preparative Device. Because of its small size, Godefroot's analytical device appeared not to be modifiable. As the model not only allowed prediction of SDE recovery of the volatile compounds but also showed the impact of the different parameters on the isolation efficiency, these observations were used to elaborate a preparative SDE (Figure 6), for which detailed schemes have been described in a recent patent.[13] The following improvements were applied.

(1) Extraction. As dynamic liquid/liquid partition coefficients, measured in the running system, were lower than those determined after equilibrium, two modifications were made.

(i) Steam and solvent vapors were condensed in separate condensers. Since extraction efficiency on the cold finger was poor, both steam and solvent condensations could be performed in two different condensers with the following advantages: use of more or less dense than water solvents without modification of the device design, no solvent revaporization by the hot steam since it is introduced into the cold part of the mixing chamber in the liquid state, and possible use of different temperatures for steam and solvent condensers.

(ii) Extraction efficiency was improved by stirring with a magnetic bar in the bottom of the steam condenser. Liquid/liquid extraction and separation of the condensed phases were achieved in two different parts (instead of the same part of the analytical device).

(2) Steam Flow. Since recovery was improved by a high steam flow, a large-diameter distillation arm was chosen.

(3) Solvent Vapors. To limit redistillation of low boiling point compounds with the solvent, a distillation column was added between the solvent flask and the condenser. The condensed solvent was then led directly to the extractor.

(4) Vacuum. Analytical vacuum SDE[7] was shown to dramatically reduce artifact generation because of sample distillation at room temperature. Due to the larger size of the preparative system, a static vacuum could not be applied. A quasi-static vacuum was maintained using a pressure controller, which opened a valve connected to the vacuum pump when the pressure increased.

(5) Separator. The phase separator was refrigerated to avoid any evaporation when working under vacuum. Its geometry was adjusted to accept solvents either heavier or lighter than water.

Solvents were tested for two different uses:

(i) Extraction at atmospheric pressure. Solvent-to-water partition coefficients were measured in the device to take into account the experimental conditions. Among the usual SDE solvents, pentane appeared less efficient than ethyl ether or dichloromethane when the mixing chamber was not stirred (Table 5). Stirring greatly improved extraction of coumarin. Dichloromethane was the most efficient solvent for atmospheric SDE with a stirred extractor.

(13) Chaintreau, A.; Maignial, L.; Pollien, P. Appareil et procédé de distillation et d'extraction simultanées. Eur. Pat. Appl. 95203496.5, 1995.
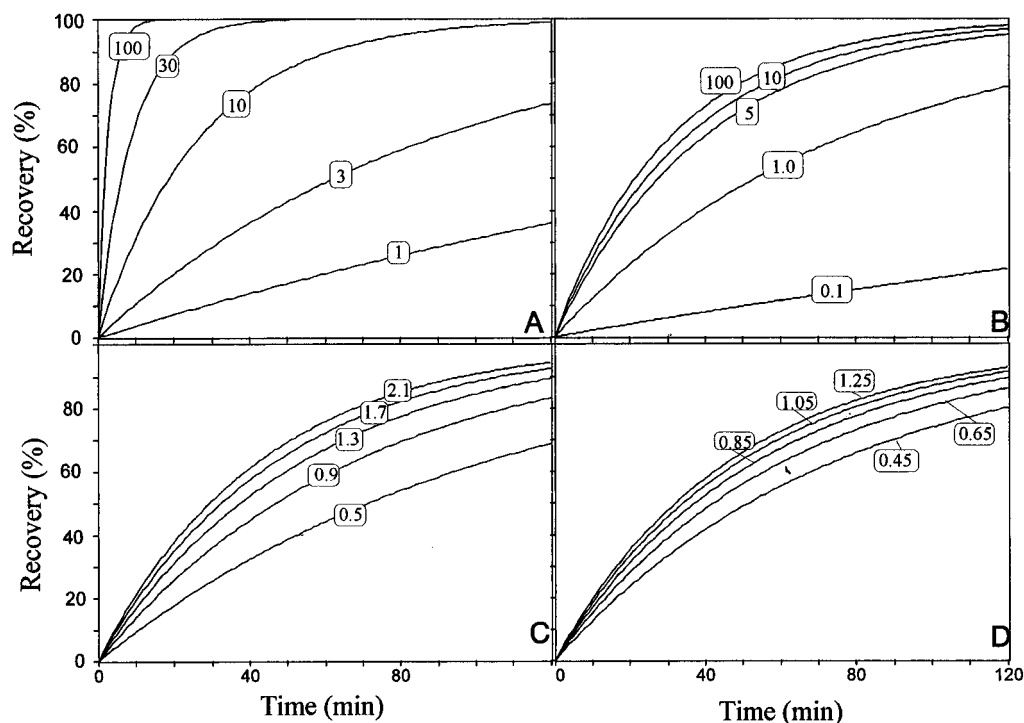
Figure 5. Simulated influence of volatility (A), liquid/liquid partition coefficient (B), solvent flow (C), and steam flow (D). (Numerical values of the corresponding parameters are indicated on the curves.)

Table 5. Solvent Characteristics

| | | K^a | | $k_s,^b$ pyridine | retention index | | boiling point |
		pyridine	coumarin		polar	nonpolar	
dichloromethane	equilib	11.5	>150	0.0084	922	513	40 °C
	unstirred	2.3	0.99				(760 mbar)
	stirred	4.0	90				
pentane	unstirred	0.31	1.0	nd	500	500	36 °C
	stirred	0.36	1.7				(760 mbar)
diethyl ether	unstirred	1.0	2.8	nd	621	500	34.5 °C
	stirred	1.1	27				(760 mbar)
isooctane	unstirred	0.26	0.9	1.79	677	685	18 °C
	stirred	0.27	1.2				(49 mbar)
toluene	unstirred	1.1	2.6	1.05	1025	751	25 °C
	stirred	2.0	17				(37 mbar)
trichloroethane	unstirred	3.4	7.4	0.42	1240	742	38 °C
	stirred	6.4	16				(39 mbar)
trichloroethylene	unstirred	1.8	6.8	0.35	972	685	10 °C
	stirred	2.6	38				(48 mbar)

[a] Solvent-to-water partition coefficient. K values at equilibrium were measured by stirring both phases and the solute until a constant concentration was observed in both solvents. [b] Air-to-solvent partition coefficient. nd, not determined.

(ii) Extraction under reduced pressure. In addition to solvents less dense than water that were tested for analytical vacuum SDE (e.g., isooctane, toluene),[7] heavier solvents were investigated as well: trichloroethane and trichloroethylene. As for atmospheric SDE, halogenated compounds seemed to exhibit better extraction properties (Table 5). As only heating temperatures were kept constant, flows were different when changing from one solvent to another because of their different latent heats of vaporization. Since solvent-to-water partition coefficients were found to be dependent on flows, the K values in Table 5 are comparable only between the stirred and the unstirred mixing chamber because flows were equal in both cases.

In conclusion, stirring the extractor dramatically improved extraction for solutes, such as coumarin, which seem to be slowly transferred from the aqueous to the organic phase. Trichloroethene appeared to be a good choice for vacuum SDE because it gave rise to the lowest redistillation, while exhibiting good extraction properties. In addition, it possessed low retention indexes compared to those of toluene and trichloroethane, and first-eluting GC peaks were less hindered than with those solvents.

Kinetics of Pyridine Preparative Recovery. Starting from the parameters given in Table 6, the theoretical model was compared with the experimental data (Figure 7). Pyridine volatility, which takes into account characteristics of the device (between 13.3 and 14.9), was found to be slightly lower than that in the analytical system (20.5). This is possibly due to the absence of reflux in the steam distillation arm, since the water returns to the sample
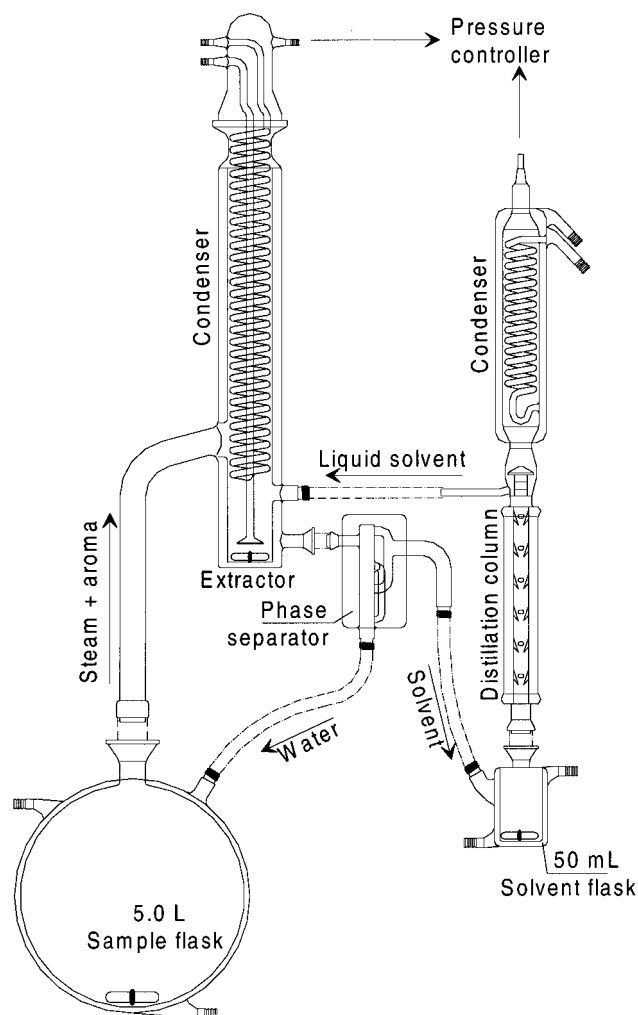
Figure 6. Scheme of preparative SDE.

Table 6. Preparative SDE Parameters Used for Kinetic Measurements (Batch at Atmospheric Pressure, Solvent CH₂Cl₂)

	W	S	k_w	k_s	K	F_w	F_s
pyridine (stirred)	2878	94	a	8.4×10^{-3}	4	5.6	2.8
coumarin (unstirred)	2774	98	0.43	0	a	5.7	6.8
coumarin (stirred)	2664	92	0.43	0	a	5.7	6.8

a Parameter adjusted by the curve-fitting program.

flask through a separate tube, contrary to Godefroot's apparatus. Consequently, under our conditions, steam distillation seems to induce less discrimination between the volatiles.

When running a SDE, a high correlation factor ($r^2 = 0.999$) was observed for $k_w = 13.5$. This value falls within the experimental volatility range previously measured (13.3–14.9). Absolute values of residuals were less than 10%, except for the first point (2.25 min), which was still close to the induction time (2.2 min). These results confirm the validity of the theoretical model.

Kinetics of Coumarin Preparative Recovery. As pyridine was easily recovered, improvement of its liquid/liquid partition coefficient had little influence on the simulated recovery curve. A kinetic study was thus performed with coumarin, which is known to be poorly recovered by SDE.[12]

At first, k_w was separately determined (0.43) by collecting condensed water into the extractor. This is higher with Gode-
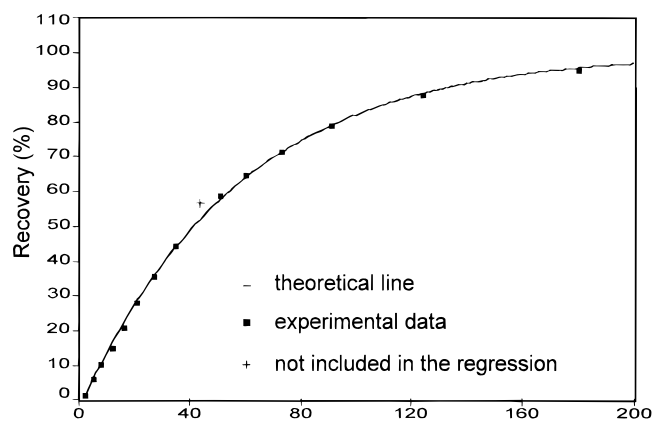

Figure 7. Pyridine recovery curve as a function of SDE time (preparative batch at atmospheric pressure, solvent CH₂Cl₂).
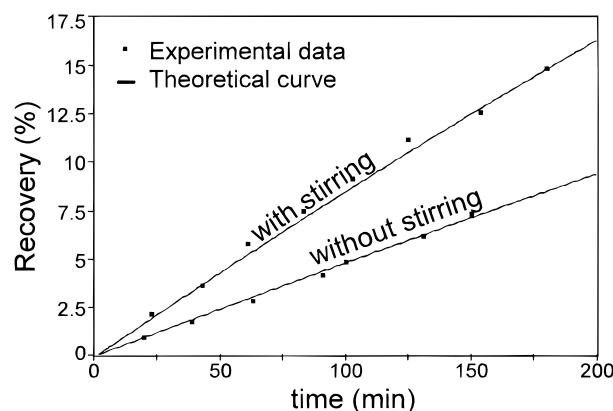

Figure 8. Influence of extractor stirring on coumarin recovery.

froot's SDE, probably for the same reasons as mentioned for pyridine: only 0.2 theoretical plate more in the analytical device than in the preparative device could explain volatility differences for both solutes.

In a first experiment, the solvent distillation column and its condenser were removed, and the solvent flask was directly connected to the water condenser, as in Godefroot's analytical device. K was measured to be 0.99 when the extractor was not stirred. This value increased up to 90 with stirring. Using a curve-fitting program and the parameters in Table 6, eq 18 was compared with experimental recoveries (Figure 8). A good correlation coefficient was found ($r^2 = 0.996$) for $K = 1.07$. This liquid/liquid partition coefficient was in agreement with that measured separately at the extractor outlet and lower than that found in the unstirred analytical device because of the greater dead volume of the preparative extractor.

In a second experiment, the system was used as shown in Figure 6, and the extractor was vigorously stirred with a magnetic bar. Equation 18 was found to best fit the experimental results ($r^2 > 0.991$) for $K > 40$ (Figure 8). Higher accuracy could not be obtained because the calculated recovery rate was not significantly increased by higher K values (Figure 9). This was already observed when simulating pyridine recovery in the analytical SDE: a low extraction efficiency strongly altered recovery, but the extraction asymptotically reached a maximum yield (Figure 9). For an optimum coumarin recovery, K must be greater than 10–15, which cannot be achieved without stirring.

CONCLUSIONS

After reconsidering simplifications of Rijks's model,[10] a new equation representing recoveries in SDE has been proposed.
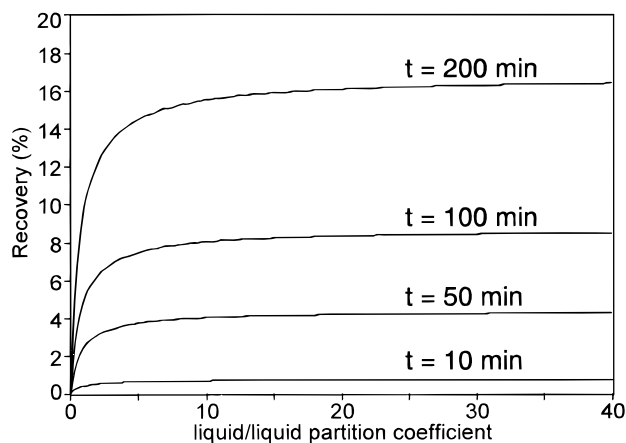
Figure 9. Influence of extraction efficiency on coumarin recovery after a given time.

Based on pyridine kinetics, this model appears to well represent operating conditions. Recovery simulations show that steam flow, extraction efficiency, and sometimes redistillation from the solvent flask are key factors influencing recovery rates. Using these results, a new preparative apparatus has been developed and optimized.

The new system allows isolation at atmospheric pressure as well as under vacuum, at room temperature, to reduce thermal degradation. The theoretical model also well represents the preparative apparatus's behavior, and the kinetics of coumarin recovery confirms the importance of an efficient extractor. Isolation yields justifying system performances will be reported in another paper, as well as the possibility of continuously feeding the sample boiler.