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ON THE DESIGN OF A SUPERCRITICAL FLUID EXTRACTION CHAMBER

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Abstract. The mixing of the supercritical fluid with the sample will fasten the SFE process where the solute diffusion in the supercritical fluid is the controlling step and the quantitative and reproducible extraction results are of great importance.

A comparative study of different extraction chambers indicates that there are several possibilities of solving the problem of the mixing of the supercritical fluid with the sample by application of the inertial mass of the supercritical fluid. Among the three different designs discussed in this study the vibrating toroidal extraction chamber seems to guarantee the most effective mixing. By means of a vertical electromagnetic actuator along with inclined spring rods combined rotating vibration of the extraction chamber is achieved. This, in its turn, generates a directed circulating movement of the supercritical fluid inside the toroidal extraction chamber. The possibility to change the vibration frequency enables to choose the most effective mixing for the sample.

The proposed design of a SFE extraction chamber is suitable for both analytical and preparative purposes. It will give the SFE system flexibility and will make choosing the most optimal conditions of SFE for different samples and purposes easy.

Key words: supercritical fluid extraction, chamber design.

INTRODUCTION

In recent years supercritical fluid extraction (SFE) has found tremendous interest among analysts [1]. As compared to the classical extraction methods the application of SFE for both analytical and preparative purposes has expanded [2]. The main advantage of SFE is the possibility to automate the whole extraction process, thus shortening the analysis time and eliminating the errors caused by the time-consuming manual sample manipulation.

SFE is a complicated process, removing the analytes from the sample requires specification of the extraction conditions, i.e. it is necessary to choose the extraction temperature and pressure, the fluid and the modifier, and to decide between the on-line or the off-line extraction mode and static or dynamic extraction [3]. To make the right decision one needs knowledge about the process kinetics and about the step that controls the speed of the whole SFE for every individual sample. As it is very clearly

pointed out by McNally [4] the maximum analyte solubility is not always needed, e.g. for the extraction of solutes at trace levels, but if there is a question of the removal of large amounts of solute from the matrix, maximum solubility will be desirable.

In the kinetic model of SFE several steps have been distinguished [4], including the analyte removal from the matrix surface, diffusion to the matrix–supercritical fluid interface, diffusion through the supercritical fluid, and solvation by the supercritical fluid.

According to [5] the extraction rate may be limited either by the desorption step or by the solution/elution step. If the extraction is limited by the kinetics of analyte transport from the solid into the extraction fluid, the rate of the extraction process will be controlled by the desorption steps. If the analyte solubility and the chromatographic retention of analytes from the solid are determining the SFE rate, the SFE process will be controlled by the solution/elution step.

Although it is possible to predict the solute solubility in a supercritical fluid [6], understanding the whole process and establishing the extraction conditions require a much deeper examination of the extraction process. In developing a quantitative SFE method much attention should be paid also to the collection step, the right choice of the restrictor, and the trapping system. This means that the choice of the extraction and collection conditions needs a careful approach and a flexible SFE system making all this possible. Only then quantitative reproducible SFE results can be expected.

Below some designs of the SFE extraction chamber are discussed that could give a possibility to regulate the SFE process in order to influence the kinetics of different steps in case it is necessary to develop an SFE method guaranteeing the maximum recovery of heterogeneous solutes and samples. The offered designs could find an application not only in the analytical but also in the preparative areas.

RESULTS AND DISCUSSION

In recent years much attention has been paid to the overall extraction process in supercritical fluid. Attempts have been made to find ways for improving extraction efficiency. SFE is considered to be a fast process, but only under certain conditions. Therefore, optimization of the extraction conditions should be accomplished first. In order to do this it is necessary to improve the analyte solubility in the supercritical fluid and the mass transfer from the matrix to the fluid and guarantee quantitative collection of the analyte in a reasonable time.

Since SFE is mostly performed in the dynamic mode [7], the analyte desorption by the supercritical fluid is considered to be fast. The determining step is the collection of the analyte from the extraction cell into the collection chamber with the fluid flow rate being one of the most important parameters.

The analyte is not distributed only over the matrix surface, but it penetrates also into the pores and the void volume inside the sample. Grinding the sample before extraction and mixing it with the supercritical fluid in the extraction chamber during extraction could give good results. As a matter of fact it is very hard to provide the sample mixing in SFE. This is the reason why sometimes dynamic extraction is performed in a closed system, where the fluid is recycled through the sample until maximum extraction is reached. This avoids the saturation of the fluid with the analyte at the matrix surface layers and also in the pores and the void room between the particles inside the sample. The disadvantage of this method is the need for an additional pump and the "memory" problem as it is very difficult to clean the extraction system due to its complicated configuration and therefore a high extraction efficiency is hard to achieve.

There is a possibility to mix the sample with the supercritical fluid by magnetic stirring with a rotor placed in the extraction chamber. The method seems to be simple, but the problem is in the thick wall of the extraction chamber body. The current induced in the wall by a changing magnetic field may heat up the extraction chamber body thus causing a deviation of the temperature from the value fixed for the extraction in the chamber during the process.

We propose different solutions for the SFE extraction chamber, which permit sample mixing in the supercritical fluid without any additional pump and magnetic stirrer. The need for more flexible extractors arose with the growth of analytical SFE, especially real samples [8]. Investigations have turned to the field of SFE methods for routine analyses of a variety of organic pollutants in natural samples. For this very careful development of sample extraction methods and an SFE extractor with great facilities for quick and comfortable change in extraction conditions are needed.

The SFE extractor should satisfy the following requirements:
– be simple to handle;
– guarantee an effective sample and fluid mixing, whereas it should allow an adjustment of the mixing conditions if necessary;
– have no "memory";
– work with extraction chambers of different size, even of preparative size;
– permit simultaneous extraction of many samples.

Our purpose was to design an SFE extractor that meets these requirements and performs fast and effective extraction, applying the inertial properties of the supercritical fluid mass for that purpose. As the main question is how to influence the interaction between the sample and the supercritical fluid inside the extraction chamber, further attention will be paid here only to its design. The supercritical fluid modification, the choice of temperature and pressure, and the analyte collection will not be discussed here.

The supercritical fluid inside the extraction chamber will develop the movement necessary for mixing indirectly, by the rotating-vibrating movement of the extraction chamber. This causes a directed movement of the supercritical fluid, and depending on the sample, in some cases also of

the sample particles. There are three possible solutions for this kind of extraction chamber:
– cylindrical extraction chamber,
– toroidal extraction chamber, and
– vibrating toroidal extraction chamber.

Cylindrical extraction chamber

The extraction chamber is a stainless steel cylindrical body with a heating element and thermosensor in it (Fig. 1). The chamber is covered with thermal insulating material. The body is fixed to the horizontal axle that is connected to the shaking mechanism. The sample is mounted into the cylindrical extraction chamber. It is recommendable to mount the powdered sample first into a porous cartridge and then place the cartridge into the extraction chamber. A restrictor (either linear or frit) with a valve for opening and closing the outlet is fixed to the extraction chamber. The extraction chamber is easily removable for cleaning and for replacing the sample.

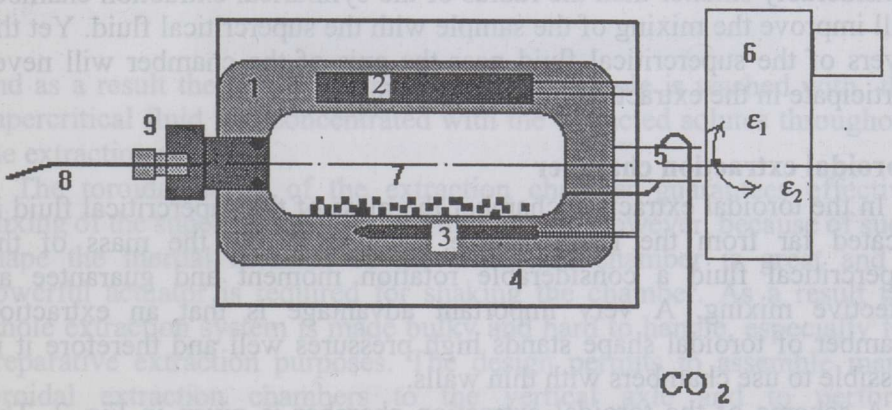

Fig. 1. Scheme of a cylindrical extraction chamber. *1*, stainless steel body; *2*, heating element; *3*, thermosensor; *4*, thermal insulating material; *5*, axle; *6*, shaking mechanism; *7*, sample; *8*, restrictor; *9*, valve.

The supercritical fluid mixing is influenced by its inertial moment. The inertial moment I of a mass-point of the supercritical fluid can be expressed by formula (1):

$$I = m r^2, \tag{1}$$

where r is the distance of the mass-point from the rotating axis.

The rotating moment M of the mass-point will be expressed by formula (2):

$$M = I e = m r^2 e, \qquad (2)$$

where e is the angular acceleration.

The angular acceleration of different magnitude in different directions given to the extraction chamber will generate rotation moments of different magnitudes, which along with the internal friction of the supercritical fluid and the friction between the supercritical fluid and the inner wall of the extraction chamber will cause directed rotation of the supercritical fluid. Owing to this directed rotation the fresh supercritical fluid or at least the one less concentrated with solutes will continuously wash the sample.

However, the efficiency of the mixing is low due to the cylindrical shape of the extraction chamber. The reason is evident from formula (2): the nearer the mass-point of the supercritical fluid is to the axis of the cylindrical extraction chamber, the smaller is its rotating moment. Therefore, the mixing of the supercritical fluid with the sample near the axis is poor. Placing the sample into a porous cartridge with a diameter considerably smaller than the radius of the cylindrical extraction chamber will improve the mixing of the sample with the supercritical fluid. Yet the layers of the supercritical fluid near the axis of the chamber will never participate in the extraction process effectively.

Toroidal extraction chamber

In the toroidal extraction chamber the mass of the supercritical fluid is located far from the rotation axle. This will give the mass of the supercritical fluid a considerable rotation moment and guarantee an effective mixing. A very important advantage is that an extraction chamber of toroidal shape stands high pressures well and therefore it is possible to use chambers with thin walls.

A scheme of the toroidal extraction chamber is given in Fig. 2. The sample is placed in a porous cartridge into the extraction chamber. At the opposite side of the chamber there is a restrictor with a valve for opening and closing the chamber outlet. Depending on its character, the sample may be placed into the extraction chamber also without a porous cartridge. This solution is acceptable in the preparative areas where routine extraction of the samples of the same kind is required. The extraction chamber is a toroidal chamber fixed to the vertical axle so that it can shake around this axle. Liquid carbon dioxide is pumped into the extraction chamber through a capillary and the pressure is raised up to the necessary level. Now a mechanical actuator for generating the shaking movement is switched on. This mechanical actuator will give through the vertical shaft the extraction chamber such a movement where the angular accelerations of the extraction chamber in different directions are different. This will cause directed movement of the supercritical fluid inside the toroidal chamber

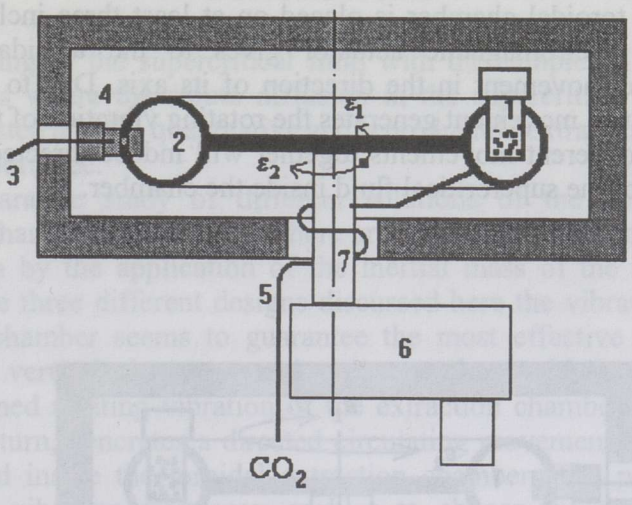

Fig. 2. Scheme of a toroidal extraction chamber. *1*, sample in a porous cartridge; *2*, extraction chamber; *3*, restrictor; *4*, valve; *5*, capillary; *6*, mechanical actuator; *7*, shaft.

and as a result the porous cartridge with the sample is washed with the supercritical fluid less concentrated with the extracted solutes throughout the extraction process.

The toroidal shape of the extraction chamber guarantees effective mixing of the supercritical fluid and the sample. However, because of such shape the inertial moment of the extraction chamber is great and a powerful actuator is required for shaking the chamber. As a result the whole extraction system is made bulky and hard to handle, especially for preparative extraction purposes. The design permits to assemble many toroidal extraction chambers to the vertical axle and to perform simultaneous extraction and mixing of several similar samples. The only problem is the massive mechanical actuator.

Vibrating toroidal extraction chamber

The vibrating toroidal extraction chamber is an improved toroidal extraction chamber. The theoretical calculations led us to the conclusion that for more effective mixing it is not enough to increase the frequency of rotating vibration and to decrease its amplitude. Therefore, combined two-dimensional movement was applied to the extraction chamber. This is achieved by means of an electromagnetic actuator whose vertical vibrating movement is transformed thanks to inclined spring rods into spiral back and forth movement of the extraction chamber. This combined movement is more effective in inducing directed circulating movement of the supercritical fluid and in some cases also the particles of the sample.

A scheme of the vibrating toroidal extraction chamber is given in Fig. 3. The toroidal chamber is placed on at least three inclined spring rods. The electromagnetic actuator gives to the toroidal extraction chamber the movement in the direction of its axis. Due to the inclined spring rods this movement generates the rotating vibration of the chamber. These two different movements together will induce directed circulating movement of the supercritical fluid inside the chamber.

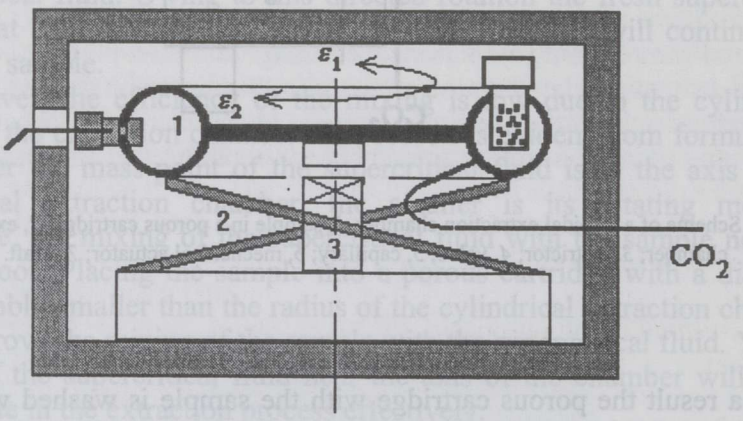

Fig. 3. Scheme of a vibrating toroidal extraction chamber. *1*, toroidal chamber; *2*, spring rods; *3*, electromagnetic actuator.

This vibrating toroidal extraction chamber has several advantages over the simple toroidal extraction chamber:
– the mixing of the supercritical fluid with the sample is more effective as in addition to rotation also vibration is applied to the supercritical fluid and sample particles;
– the electromagnetic actuator is comfortable to handle and easy to produce;
– the variation of vibration frequency is easy;
– it is easy to find the optimal mixing for the sample by changing the vibration frequency;
– the extraction chamber is compact and less massive than the simple toroidal extraction chamber, therefore it may be used both for analytical and preparative extraction purposes.

CONCLUSIONS

The mixing of the supercritical fluid with the sample will fasten the SFE process where the solute diffusion in the supercritical fluid is the controlling step and the quantitative and reproducible extraction results are of great importance.

A comparative study of different solutions of the design of the extraction chamber indicates that there are several possibilities of solving the problem by the application of the inertial mass of the supercritical fluid. Of the three different designs discussed here the vibrating toroidal extraction chamber seems to guarantee the most effective mixing. By means of a vertical electromagnetic actuator along with inclined spring rods combined rotating vibration of the extraction chamber is achieved. This, in its turn, generates a directed circulating movement of the supercritical fluid inside the toroidal extraction chamber. The possibility to change the vibration frequency enables to choose the most effective mixing for the sample.

The proposed design of an SFE extraction chamber is suitable for both analytical and preparative purposes. It will give the SFE system flexibility and will make it easy to choose the most optimal conditions of SFE for different samples and purposes.

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REFERENCES

1. Camel, V., Caude, M. & Tambuti, A. SFE of an organophosphorus compound from soils with capillary GC analysis. *J. Chrom. Sci.*, 1995, **33**, 3, 123–132.
2. Greibrokk, T. Application of supercritical fluid extraction in multidimensional systems. *J. Chromatogr.*, 1995, A 703, 523–533.
3. Bowadt, S. & Hawthorne, S. B. Supercritical fluid extraction in environmental analysis. *J. Chromatogr.*, 1995, A 703, 549–571.
4. McNally, M. E. P. Advances in environmental SFE. *Anal. Chem.*, 1995, **67**, 9, 308A–315A.
5. Hawthorne, S. B., Galy, A. B., Schmitt, V. O. & Miller, D. J. Effect of SFE flow rate on extraction rates: Classifying sample extraction behavior. *Anal. Chem.*, 1995, **67**, 2723–2732.
6. Miller, D. J. & Hawthorne, S. B. Determination of solubilities of organic solutes in supercritical CO_2 by on-line flame ionization detection. *Anal. Chem.*, 1995, **67**, 273–279.
7. Yang, Y., Hawthorne, S. B. & Miller, D. J. Estimating flow-rates for sub- and supercritical fluid extractions with linear restrictors. *J. Chromatogr.*, 1995, A 690, 131–139.
8. Bowadt, S., Johansson, B., Wunderli, S., Zenning, M., De Alencastro, L. F. & Grandjean, D. Independent comparison of Soxhlet and supercritical fluid extraction for the determination of PCBs in an industrial soil. *Anal. Chem.*, 1995, **67**, 2424–2430.

SUPERKRIITILISE FLUIDUMEKSTRAKTORI EKSTRAKTSIOONIKAMBRI KONSTRUKTSIOONIST

Toomas SÕMER, Karin PUNNING

Superkriitilise fluidumi segamine ekstraheeritava prooviga ekstraktsiooniprotsessi käigus kiirendab ekstraktsiooni juhtudel, kus ekstraheerunud aine difusioon fluidumis kontrollib kogu protsessi kiirust.

Ekstraktsioonikambri konstruktiivsete lahenduste võrdlemine näitab, et superkriitilise fluidumi ja ekstraheeritava proovi segamiseks on võimalik rakendada fluidumi inertsmassi. On analüüsitud kambri kolme konstruktsiooni. Selgub, et kõige efektiivsema segamise tagab vibreeriv toroidaalne ekstraktsioonikamber. Vertikaalse elektromagnetilise ajami ja kaldvarrasvedrude abil tekitatakse ekstraktsioonikambri pöördvõnkumine, mis omakorda põhjustab superkriitilise fluidumi suunatud tsirkuleeriva liikumise toroidaalse ekstraktsioonikambri sees. Vibratsiooni sageduse ja amplituudi muutmine võimaldab iga proovi puhul valida kõige efektiivsema segamise.

Vibreerivat toroidaalset ekstraktsioonikambrit on võimalik kasutada nii analüütilistel kui ka preparatiivsetel eesmärkidel. Selline kamber muudab superkriitilise fluidumekstraktori süsteemi suhteliselt paindlikuks, s. t. erinevate proovide ja eesmärkide jaoks on lihtne valida kõige optimaalsemaid ekstraktsioonitingimusi.