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An eco-friendly efficient extractor

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Abstract

A microscale solid–liquid Pyrex extractor is described. The extractor has a novel detachable extraction vessel (H) containing a filter paper cylinder (C) over the reservoir. A filter paper cylinder (C) is firmly placed in the socket (E) with a plug (G) on which the cylinder has been placed. The sample is directly weighed in the extraction vessel (H) and the vessel is clamped (F) to the body (B). Contents in the extraction reservoir (H) are stirred (I) with a magnetic stirrer (J) and heated sufficiently (e.g. at 84.8 °C in using water) by the solvent vapor (D). Easy filtration (C) and continuous outflow (D) of the filtrates out of the reservoir (H) keeps a stable boiling condition (K), rather than batchwise conditions operative in a Soxhlet; this results in rapid and exhaustive extraction. The present extractor (8.0 mL extraction reservoir (H) capacity) equipped with a 25 mL solvent flask (K) was applied to fat extraction from powdered peanut by using 18 mL of ether. The extraction was complete in 30–60 min depending on reflux rate; in contrast, extraction with a commercial micro-Soxhlet device (23.9 mL extraction reservoir capacity) equipped with a 25 mL flask by using 34 mL of the solvent was incomplete in 120 min. Unlike filter paper thimbles used in Soxhlet devices, filter paper cylinder (C) in the new extractor could be reused many times and results in significant savings of the filter paper cylinders. Small reservoir and flask capacities of the new extractor minimize the use of organic solvents. The present apparatus permits fast and efficient extraction, sharply reduces waste, minimizes solvent consumption, and thus should find wide use aiming at the Green Solutions to Global Problems.

Keywords: Eco-friendly microscale solid–liquid Pyrex extractor; Detachable extraction vessel; Stirred and heated extraction; Fast and efficient extraction; Filter paper cylinder reused; Solvent consumption minimized; Fat extraction from powdered peanut

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1. Introduction

For 126 years, Soxhlet extraction has been the most used technique for isolation of organic analytes from solid samples [1]. The most significant shortcoming of Soxhlet extraction is the lengthy time requirement for the quantitative extraction that can be 8 h [2], 16 h [3] and practically 24 h or more hours [4], and results in wasting time, electricity, water and solvents. This time requirement makes it labor-intensive and limits the number of samples that can be processed. Both large amounts of organic solvents and the boxes of filter paper thimbles are also required and wasted, which are not only expensive to dispose of but which may cause environmental pollution themselves.

Recently, there has been pressing interest in the concepts of Green Solutions to Global Problems [5]. Numerous other extraction techniques have been used to extract analytes from solid samples. Commercial automated Soxhlet devices, which obtained a significant reduction of extraction times with boiling and rinsing steps, but still requires large amounts of solvents and large number of filter paper thimbles. Soxwave is similarly a commercial device that uses microwave energy to make easier the rupture of the analyte-matrix bonds. Focused microwave-assisted Soxhlet device was also developed in 1998 [6]. The main drawback of microwave use is its dependence on the extractant dielectric constant. Therefore, efficient extractions are only expected with polar solvents. Initial cost of these devices is high.

Supercritical fluid extraction (SFE) replaces hazardous solvent consumption and is environmentally safe because it uses carbon dioxide as the extractant. However, there are sev-

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eral disadvantages to SFE. CO_2 is non-polar, which limits its uses, the extracted oil is less stable and subject to oxidation and initial cost and maintenance of equipment are high [7,8].

Microwave-accelerated extraction, which still requires large amounts of solvent, greatly reduces extraction times accelerating the extraction in a sealed vessel under temperature-elevated conditions above the atmospheric boiling point of solvent [9]. However, this method becomes labor-intensive because samples must cool before further processing. The analyst must then filter, centrifuge or decant the samples to quantitatively separate the extract from the solid material. Time saved due to the fast microwave extraction is lost in the cooling process, re-extraction and preparation of the analyte for further analysis [10]. Initial cost and maintenance of equipment are high because of the redundant safety features, which act as a backup to prevent a possible fire or explosion from occurring inside the cavity.

Another extraction technique is accelerated solvent extraction (ASE) [10,11]. This technique also uses pressure and temperature to accelerate extraction from solid samples. It greatly reduces extraction time. Automation can be achieved to extract analyte from different matrices. However, this technique still requires large volumes of solvent for quantitative extraction compared with the solvent reflux technique in Soxhlet and the initial cost of equipment including an HPLC pump is prohibitive for most laboratories.

Obviating the main shortcomings of the conventional Soxhlet device, laboratory affordable solid–liquid Pyrex extractors were developed for rapid extraction by the Miyamoto and Nara in 1982–1985 [12–14]. A filter paper thimble or cylinder was arranged over the extraction reservoir and contents in the reservoir were exhaustively stirred with a magnetic stirrer, and sufficiently heated by solvent vapor to increase extraction efficiency remarkably. The main drawback of these improved extractors was the difficulty of sample weighing manipulation into the extraction reservoir.

In the present paper, a novel eco-friendly microscale solid–liquid Pyrex extractor, which permits easy manipulation for sample weighing directly in the extraction vessel, fast and efficient extraction, reuses filter paper cylinder many times, minimizes solvent consumption, and thus should find wide use, has been proposed.

2. Experimental

2.1. Instrument and procedure

Fig. 1 shows the microscale extractor unit, which has a novel detachable extraction vessel (H) containing a filter paper cylinder (C) over the reservoir (H). A filter paper cylinder (C), which is firmly placed in the socket (E) with a plug (G) on which the cylinder has been placed, can be reused many times. The sample is directly weighed in the extraction vessel/sample weighing dish (H) and then the vessel is clamped (F) to the body (B). Solvent is easily delivered with a homemade dispenser without exposure to volatile solvent in the extraction reservoir (H) and the solvent flask (K) via the head of the condenser (A). Contents in the extraction reservoir (H) are continuously stirred (I) with a magnetic stirrer (J) and heated sufficiently by the solvent vapor (D). Easy filtration (C) and continuous outflow (D) of the filtrates out of the reservoir (H) keeps a stable boiling condition (K) rather than batchwise conditions operative in a Soxhle, this results in rapid and efficient extraction. It is also lab-worker friendly that agitation of the sample–solvent suspension with a magnetic stirrer does not make noise. Arrangement of the filter paper cylinder over the extraction vessel provides the automatic separation of the extract during the extraction step without require troublesome manual filtration step. After completing the quantitative extraction, the filter paper cylinder (C) and the extraction vessel (H) are thoroughly cleansed with plenty of condensed pure solvent. Waste solvent in the reservoir (H) is also easily emptied with a homemade suction collection device by inserting its suction tube into the reservoir (H) via the head of condenser (A) without expo-

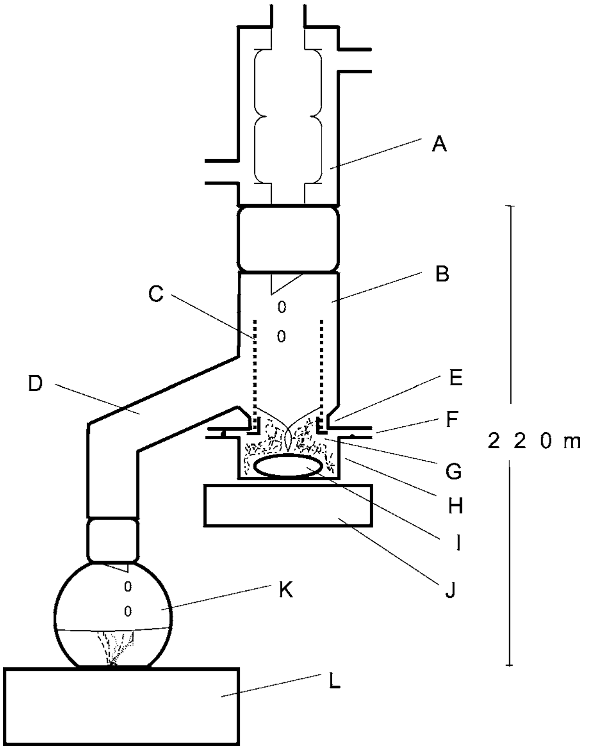

Fig. 1. Scheme of eco-friendly efficient extractor: constructed of Pyrex glass. (A) Allihn condenser, (B) extractor body, (C) filter paper cylinder, cellulose fiber, size 20 mm × 60 mm, (D) solvent vapor/extract outflow tube, (E) socket for filter plug, (F) o-ring, Kalrez® 4079, securely held with a steel clamp, Keck, KC29, to form a leak-tight seal, (G) filter plug, Teflon, (H) sample weighing dish/extraction vessel, 8.0 mL practical capacity, (I) stirrer magnet, Teflon, 15 mm length, (J) magnetic stirrer, (K) solvent flask, 25 mL nominal capacity and (L) aluminum heating block, 160 W, or heating mantle, 100 W, regulated by a voltage controller.

sure to volatile solvent. Then the extraction vessel (H) can be detached and easily be rinsed for its repeated use. It is easy to clean up the o-ring (F) with a toothbrush.

Crude fat determination of powdered peanut was attempted using standard procedures [2,3]. Commercial micro-Soxhlet device equipped with a 25 mL solvent flask was used under the same heating condition as in the proposed extractor equipped with a 25 mL flask. Diethyl ether, guaranteed grade, is used for extractant. Filter paper thimbles and cylinders and commercially available powdered peanut were dried at 105 °C for 2 h immediately before use. Filter paper cylinder, as it was placed in the extractor body, was also dried with hot air for 10 min for its repeated use. Sample size was 0.2–0.5 g. An ordinary single-pan or substitution balance (capacity 200 g, standard deviation 0.1 mg) was used to weigh precisely small amounts of sample in a glass weighing dish and extracted crude fat in a 25 mL flask because of its constant sensitivity. Temperature within the extraction reservoir was measured for 30 min by inserting a thermocouple thermometer probe via the head of condenser into the extraction reservoir in each extractor. Room temperature was at 20 ± 1 °C.

3. Results and discussion

3.1. Eco-friendly efficient extraction

The present extractor (8.0 mL extraction reservoir practical capacity) equipped with a 25 mL solvent flask was applied to fat extraction from powdered peanut by using 18 mL of diethyl ether. Fig. 2 shows that the proposed extraction was complete in 30–60 min depending on reflux rate; in contrast, extraction with a commercial micro-Soxhlet device (23.9 mL extraction reservoir practical capacity) equipped with a 25 mL flask by using 34 mL of the solvent was incomplete in 120 min, and may result in the lengthy time requirement for the quantitative extraction. Totally different approach to each equilibrium was observed and also highly significant difference between mean values is stated at the 1% level, as shown in Table 1. In this technique, the only differences are direct contact between sample and solvent and exhaustive agitation of the sample–solvent suspension at elevated temperatures to accelerate analyte migration from sample to solvent. The temperature of the sample–extractant suspension in this extraction reservoir is definitely higher than in conventional micro-Soxhlet and close to the boiling point of the solvent of choice (e.g. at 84.8 °C in using water) as shown in Table 2. These two factors, i.e. agitation and elevated temperatures may account for the significant reduction in extraction time compared with the conventional Soxhlet extraction technique. Statistical analysis of the additional experimental results plotted in solid circles in Fig. 2 shows the third factor that the greater the reflux rate of solvent leads to the shorter time required to replace the extract in the extraction reservoir with condensed pure solvent as illustrated in the following section. After completing the quantitative extraction, the filter paper cylinder and the extraction vessel are thoroughly cleansed with plenty of condensed pure solvent. Table 3 shows that unlike filter paper thimbles used in Soxhlet devices, filter paper cylinder in the new extractor could be reused many times with no effect on accuracy and precision and results in significant savings of the filter paper cylinders. In order to sharply reduce the cartridge garbage for the Green Solutions, it is only required to easily rinse the detached extraction vessel without requiring a full-scale washing and dry the extraction vessel and the filter paper

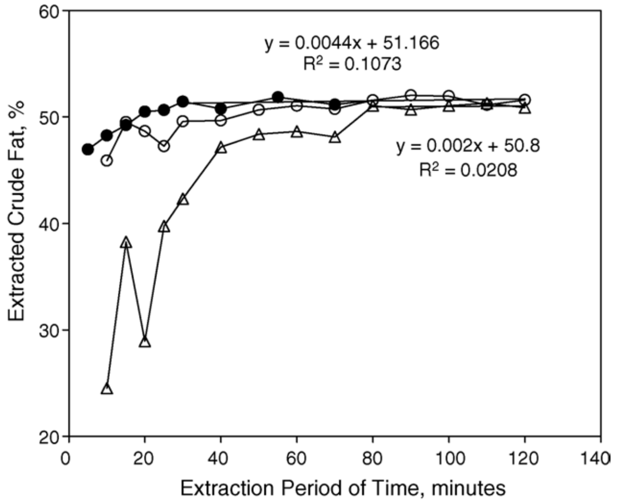

Fig. 2. Dependence of yield on extraction period in ether extraction of crude fat from powdered peanut: (◯) proposed micro-extractor with 8.0 mL reservoir capacity; (△) micro-Soxhlet with 23.9 mL reservoir capacity, ether reflux rate in both extractors: 2.0 mL/min (25 mL flask, 160 W-aluminum block heater, at 55 V). Additionally, (●) proposed micro-extractor, ether reflux rate: 8.2 mL/min (25 mL flask, 100 W-heating mantle, at 75 V). Proposed technique: inclinations of regression lines ($y = 0.0044x + 51.166$ for 30–120 min and $y = 0.01x + 50.547$ for 60–120 min) from x-axis are insignificant, but only significant at the 40% level. Micro-Soxhlet: inclination of regression line ($y = 0.002x + 50.800$ for 80–120 min) from x-axis is insignificant even at the 50% level.

Table 1
Experimentally determined crude fat values in powdered peanut with micro-Soxhlet and proposed extractions for 80–120 min

Extraction period of time (min)	Crude fat (%)	
	Micro-Soxhlet	Proposed extractor[a]
80	51.072	51.579
90	50.700	52.034
100	51.068	51.967
110	51.282	51.128
120	50.880	51.610
Mean ± S.D.	51.00 ± 0.22 (98.72%)	51.66 ± 0.36 (100%)

Experimental details of this experiment are found in Fig. 2. Difference between uncertainties not stated at the 5% significance level. Difference between mean values highly significant at the 1% level.

[a] Inclination of the regression line ($y = -0.0084x + 52.504$ for 80–120 min) from x-axis is insignificant even at the 50% level; no significant drift and uncertainty found with experimentally determined values on successive reuse of easily rinsed extraction vessel.

Table 2
Experimentally determined temperature values inside extraction reservoirs of micro-Soxhlet and proposed extractor

Solvent	Extraction temperature of micro-Soxhlet[a] (°C)	Extraction temperature of proposed extractor[b] (°C)	Boiling point of solvent [15]
Diethyl ether[c]	33.2–34.3	34.0	34.6
Ethanol[d]	58.4–65.3	73.8	78.3
Water[e]	68.4–79.2	84.8	100.0

[a] Representative temperatures, changed repeatedly from minimum to maximum synchronizing with siphonage.

[b] Equilibrium temperature inside stirred reservoir.

[c] In 25 mL flasks, 100 W-heating mantles, at 75 V.

[d] Same conditions, at 90 V.

[e] Same conditions, at 100 V.

Table 3
Filter paper cylinder reusable for extraction of crude fat from powdered peanut with the proposed extractor

Experimentally determined crude fat (%)			
Extraction period of time (min)	Filter paper used once[a]	Extraction period of time (min)	Filter paper reused successively[b]
80	51.57_9	120	51.74_8
90	52.03_4	120	52.29_7
100	51.96_7	120	50.95_9
110	51.12_8	120	51.53_0
120	51.61_0	120	51.35_6
Mean ± S.D.	51.66 ± 0.36		51.58 ± 0.50

Difference between uncertainties not stated at the 5% significance level. Difference between mean values not stated even at the 50% level.

[a] Ether reflux rate 2.0 mL min^{-1} (160 W-aluminum block heater, at 55 V).

[b] Ether reflux rate 4.6 mL min^{-1} (100 W-heating mantle, at 55 V). Filter paper cylinder, as it was placed in the extractor body, was dried with hot air for 10 min for its reuse. No significant drift and uncertainty found with experimentally determined values on successive reuse of filter paper cylinder.

cylinder, as it is placed in the extractor body, for their repeated use. Continuous outflow of the filtrates out of the extraction reservoir leads to minimizing the reservoir and flask capacities and the use of organic solvents (18 mL ether required) in the new extractor rather than batchwise conditions operative in a micro-Soxhlet (34 mL required). The present work uses less than one-fifth the ether (100 mL) generally required in the regular Soxhlet device (72.0 mL extraction reservoir practical capacity) equipped with a 150 mL solvent flask. The proposed extraction technique has no change in the solvent scheme compared with the traditional Soxhlet technique, except that Kalrez® 4079 o-ring to form a leak-tight seal of the detachable extraction vessel is not recommended for applications involving water steam, aliphatic amines, ethylene oxide or propylene oxide. After the extraction step, concentration of smaller amount of the extract in the proposed technique can be performed definitely faster over an evaporator. Dilution of the extract to a fixed volume for quantitation of analytes can also be directly carried out by using a specialty Pyrex (borosilicate) glass volumetric solvent flask, with which the present extractor is equipped, without transfer the extract to other volumetric flask, with no volumetric effect by heating the flask (e.g. repeatedly at 150 °C for 60 min [13] or even at 320 °C for 168 h [16]).

3.2. *Times for analyte elution and extract replacement*

In this technique, times required to elute the analytes from solid sample to solvent and required to replace the extract in the reservoir with condensed solvent after the elution is complete can be calculated from measurements of quantitative extraction periods of time and solvent reflux rates.

Time required for quantitative extraction t_{extr} is given by the relation

$$t_{\mathrm{elu}} + t_{\mathrm{repl}} = t_{\mathrm{extr}} \tag{1}$$

where t_{elu} is the time required for analyte elution from solid sample to solvent and t_{repl} is the time for replacement of the extract with condensed solvent after the elution is complete. On the contrary, t_{repl} is given by the following relation [13]

$$t_{\mathrm{repl}} = \left(\frac{V_{\mathrm{c}}}{v}\right) \ln\left(\frac{m_0}{m_{\mathrm{r}}}\right) \tag{2}$$

where capacity of the extraction reservoir $V_{\mathrm{c}} = 8.0$ mL, initial amount of solute contained in the reservoir $m_0 = 100$ and residual amount of solute in the reservoir at a time of 99.99% replacement of the extract $m_{\mathrm{r}} = 0.01$.

Using Eqs. (1) and (2) with experimentally measured solvent reflux rate $v = 2.0\,\mathrm{mL\,min^{-1}}$ and $t_{\mathrm{extr}} = 60$ min, we obtain

$$t_{\mathrm{repl}\,99.99\%} = 36.8\,\mathrm{min}, \qquad t_{\mathrm{elu}} = 60 - 36.8 = 23\,\mathrm{min}$$

With higher reflux rate $v = 8.2\,\mathrm{mL\,min^{-1}}$ and $t_{\mathrm{extr}} = 30$ min, we obtain a definite t_{elu} value for a specific sample, powdered peanut, to be ∼22 min.

$$t_{\mathrm{repl}\,99.99\%} = 8.98\,\mathrm{min}, \qquad t_{\mathrm{elu}} = 30 - 8.98 = 21\,\mathrm{min}$$

4. Conclusions

This detachable extraction vessel system resulted in simple construction of efficient solid–liquid Pyrex extractor with the arrangement of the filter paper cylinder over the extraction vessel, requiring minimal manipulations for sample weighed directly in the reservoir. The present apparatus permits low initial investment, fast and efficient extraction, and sharply reduces waste, minimizes solvent consumption, and thus should be remarkably cost-effective and find wide use aiming at the Green Solutions to Global Problems.

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