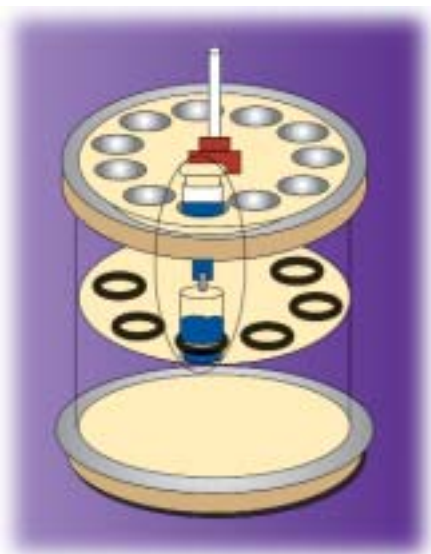


# Microwave-Assisted Organic Extraction and Evaporation: An Integrated Approach



The authors describe the development of a novel technique, integrated microwave extraction, which is an enhanced version of microwave-assisted solvent extraction. In the technique, solvents are optimized for chemistry, and microwave absorption is modified using secondary microwave absorbers enabling traditional solvent applications. The salient features of integrated microwave extraction are its equipment integration and secondary heating technology, which are designed to overcome the deficiencies of microwave-assisted solvent extraction. The authors' comparative studies of integrated microwave extraction with traditional extraction techniques indicate equivalent recoveries for both polar and nonpolar solvents within a 95% confidence interval.

**A**nalyzing samples for organic analytes usually involves two major steps: sample preparation and instrumental quantitation. Advances in analytical chemistry have led to the development of instruments that have extremely low detection limits and high sample throughput. In comparison, progress in sample preparation has lagged behind in sophistication and instrumentation. Although analysis can be performed in a few minutes, sample preparation can require hours or days for completion. Two-thirds of analysis time typically is spent on sample processing (1). Another significant aspect of sample preparation is its contribution to analytical error. The accuracy and the precision of data generated often are more dependent upon the operations performed on the sample before analysis rather than upon the measurement itself. Sample processing typically accounts for approximately 30% of the error generated during the entire analytical method. Operator error generally accounts for roughly 20%. Thus, improving and automating sample preparation can decrease error by as much as 50% (1).

Sample preparation for organic analysis usually involves extracting the analyte of interest from the matrix into an appropriate

solvent. The most widely used extraction techniques are Soxhlet, shake-filter, and sonication. These methods are labor-intensive, single-sample (per apparatus) techniques that involve the use of large quantities of solvents, which often must be evaporated to concentrate the analyte before analysis. Some Soxhlet extractions can take several hours or days. Another disadvantage of these methods is the increased operating costs associated with the disposal of hazardous waste solvents. The filtration and sample transfer steps, which often are mandatory, also represent a potential source of error from analyte loss.

Microwave-assisted solvent extraction has overcome most of these shortcomings. The use of microwave-enhanced chemistry, the theory of which has been discussed extensively (2,3), offers many advantages over traditional heating methods. Closed-vessel microwave extraction allows extraction solvents to be heated rapidly to temperatures two- or threefold higher than their atmospheric boiling points, which results in shorter extraction times (10–30 min). The amount of consumed solvent is therefore considerably less (20–30 mL). Stirring is possible, and it makes the extraction conditions more homogenous, promotes interac-

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tion with the solvent, and assists in releasing analytes from the matrix.

However, microwave-assisted solvent extraction has some inherent drawbacks that must be overcome to allow for its widespread use. A chemical compound will absorb microwave energy roughly in proportion to its dielectric constant; that is, the higher the value of the constant, the higher the amount of energy absorbed (2). Because organic extractions typically involve nonpolar solvents with very small, if any, dielectric constants, a polar cosolvent often must be used to aid heating of the solution (4). The use of a polar cosolvent led to the extraction of a broader spectrum of compounds, in addition to the analytes of interest, and created potential interference problems during

analysis. Further, microwave-assisted solvent extraction does not preclude the traditional processing steps of filtration and evaporation.

This article describes the development of a technique called *integrated microwave extraction*, which is designed specifically to overcome these deficiencies. Integrated microwave extraction combines the processes of extraction, filtration, evaporation, and solvent recovery through the use of integrated hardware that overcomes some traditional limitations. Using a microwave-absorbing component makes nonpolar solvents compatible for microwave extraction (Figure 1). Although this article describes using integrated microwave extraction for determining polynuclear aromatic hydrocarbons (PAHs) and pesticides in soils, the process and equipment described are applicable to various matrices.

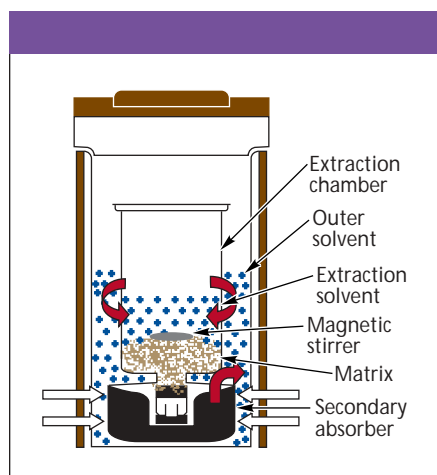
### Experimental

**Instrumentation: Microwave extraction and evaporation systems:** We used an Ethos SEL integrated microwave-assisted solvent extraction system (Milestone Inc., Monroe, Connecticut) for this work. This system comprised an Ethos laboratory microwave unit with a built-in magnetic stirrer, a fiberoptic temperature sensor, and a solvent sensor. The sample rotor was a basic 12-position extraction rotor with 100-mL, fluoropolymer-lined, 4-nitro-3-(trifluoromethyl)phenol vessels that had a maximum operating temperature and pressure of 220 °C and 30 bar (500 psi), respectively. The need for a polar cosolvent was elimi-

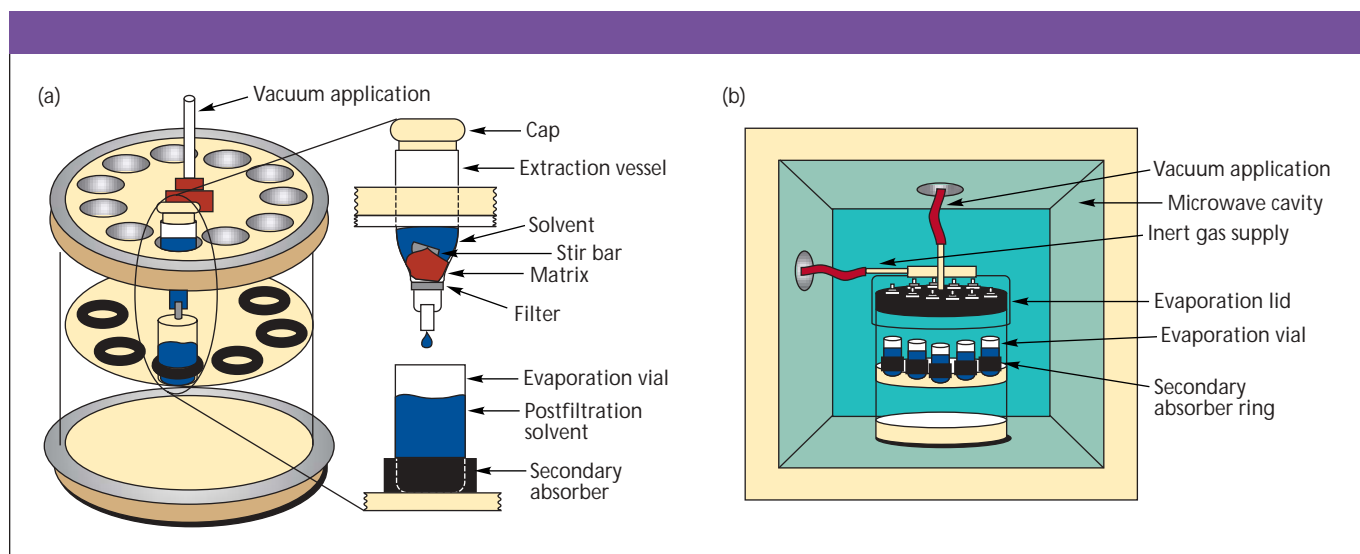
nated by the incorporation of a secondary microwave absorber that is a chemically inert, microwave-absorbing fluoropolymer (Figure 1). Postextraction filtration and evaporation was performed using a FiltEX filtration system (Figure 2a) and an EvapEX evaporation system (Figure 2b) (both from Milestone) without transferring the extracts. The evaporated solvent was collected and recycled using the evaporation system and a solvent recovery system. We used EasyWave control software (Milestone) to monitor and control the microwave system. We were able to change the microwave parameters during the run, which enabled real-time optimization during method development.

**Analysis:** PAH analysis was performed using a Saturn gas chromatography–mass spectrometry (GC–MS) system (Varian Inc., Walnut Creek, California), and the pesticide analysis was performed with a gas chromatograph (Shimadzu Scientific Instruments, Columbia, Maryland) equipped with a flame ionization detector.

**Method: Microwave extraction:** We prepared the extraction vessels by fitting them into the secondary absorber base and inserting a suitable filtering medium — filter papers, frits, membranes, or glass wool — into the vessels. For the 100-mL extraction chambers, we prepared the sample in the following manner: We placed 1–5 g of a certified reference material soil sample (RTC, Laramie, Wyoming) into the extraction chambers with 10–15 mL of solvent. The extraction chambers contained the same solvent as the extractant and had enough volume (~20 mL) to immerse the secondary



**Figure 1:** Cross-section of an assembled vessel depicting the mechanism of secondary absorbing technique.



**Figure 2:** Depiction of equipment configuration. Shown are (a) the filtration system and (b) a cross-sectional view of the microwave cavity and the evaporation system.

absorber base and part of the vessel. We recycled this solvent for subsequent runs. We capped the vessels with polytetrafluoroethylene (PTFE) lids to separate the inner and outer solvents and added glass-coated magnetic stir bars. The stirring action was set to 40% of maximum. We sealed the closed extraction chambers into the individual rotor segments.

The soil samples were extracted using a 5-min ramp to 100 °C and a 15-min hold at 100 °C. After cooling to 25 °C, we opened the extraction chambers and removed the vessels. We snapped off the secondary absorber base and fitted the vessel directly into the slot in the filtration system lid. We vacuum filtered the samples into vials in which evaporation subsequently was performed. Figure 2a shows that the vacuum was applied in the central position. After completing the filtration, we replaced only the closure from the filtration system with the evaporation closure.

**Microwave-assisted evaporation:** We evaporated the solvent under argon using alternate heating and cooling steps of 700 W for 2 min and 0 W for 30 s. Figure 2b shows the evaporator connected at the central position. We added a cooling step to avoid possible overheating of analytes, which could cause thermal degradation. We repeated this cycle four or five times, depending upon the solvent used.

## Results and Discussion

We tested the solvents' effect upon the extraction of PAHs. The data we obtained indicate analogous results between the two classes of solvents (Figures 3 and 4). For

example, for pyrene, acetone extracted 2715  $\mu\text{g/g} \pm 357 \mu\text{g/g}$ , and hexane extracted 3025  $\mu\text{g/g} \pm 106 \mu\text{g/g}$  (95% confidence limit,  $n = 6$ ). The acetone recovery of fluoranthene was 3359  $\mu\text{g/g} \pm 353 \mu\text{g/g}$ , and the hexane recovery was 3831  $\mu\text{g/g} \pm 107 \mu\text{g/g}$  (95% confidence limit,  $n = 6$ ). Although the data indicate statistically equivalent recoveries for both classes of solvents, the hexane extracts demonstrated an increase in average recoveries. We also observed that hexane extracts provided cleaner chromatograms and spectra than the polar solvents. Therefore, we concluded that nonpolar solvents could replace solvent combinations.

The secondary microwave absorber base converted the microwave power to thermal energy and transferred this energy to the surrounding solvent, which in turn heated the extracting solvent inside the glass extraction chamber. Figure 1 illustrates this secondary heating mechanism. The ability to use either type of solvent enabled us to tailor the extraction conditions to the analyte of interest or to mimic the extraction conditions used in traditional methods. We also observed that recoveries using integrated microwave extraction were comparable to those reported for the certified reference materials, which were obtained using Soxhlet extraction.

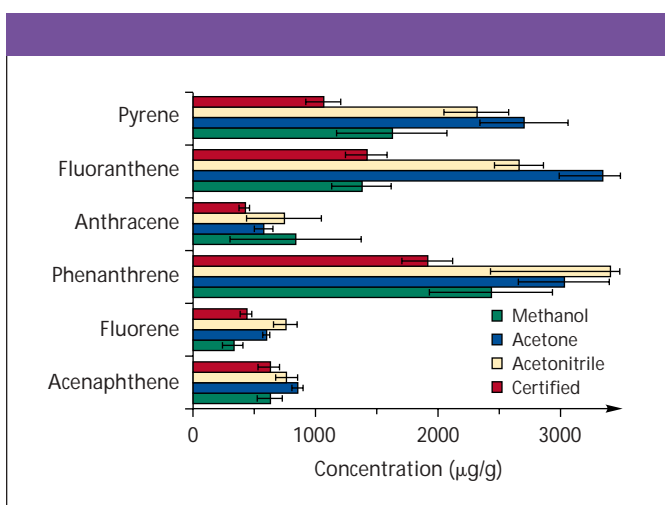
Because the extraction process included no transfer steps, the error associated with each transfer step might have been eliminated, which is evident from the higher precision values associated with the integrated microwave extraction. To be accepted as a replacement for the traditional techniques,

the results obtained from the method must be comparable to those obtained from traditional methods. Therefore, we extracted pesticides using a 1:1 hexane-acetone (v/v) mixture to simulate the Soxhlet extraction procedure closely (Figure 5). The results illustrated good agreement between integrated microwave extraction and certified values, but the microwave extraction required approximately one-fiftieth the amount of time needed for Soxhlet extraction. We extracted 12 samples simultaneously in 15 min.

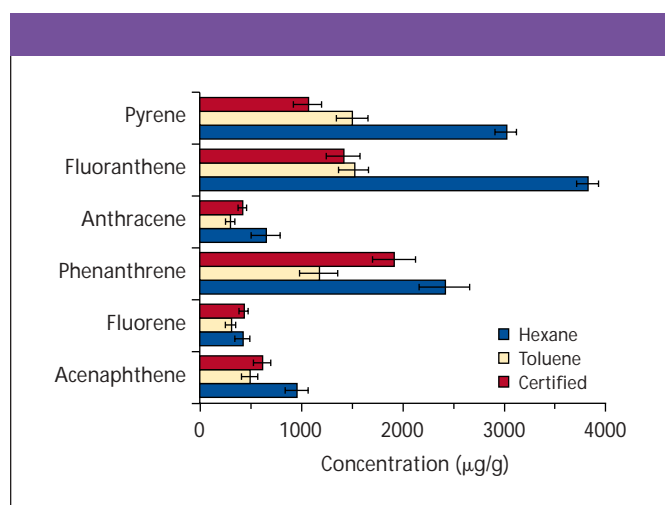
Using a microwave for evaporation allowed good control over the evaporation conditions. The microwave power output was varied to produce slow heating, even with small solvent volumes (<2 mL). The results from evaporation recovery of PAHs in hexane verify complete recovery of the analytes in which the analyte concentration was 10–30  $\mu\text{g/mL}$  each (Figure 6). When subjected to GC-MS analysis, the recovered solvent showed no analyte loss, so the solvent could be recycled. Shah and co-workers (5) performed a comparative analysis of integrated microwave versus Soxhlet extraction. Table I lists time and solvent consumption associated with processing 1000 samples.

## Conclusion

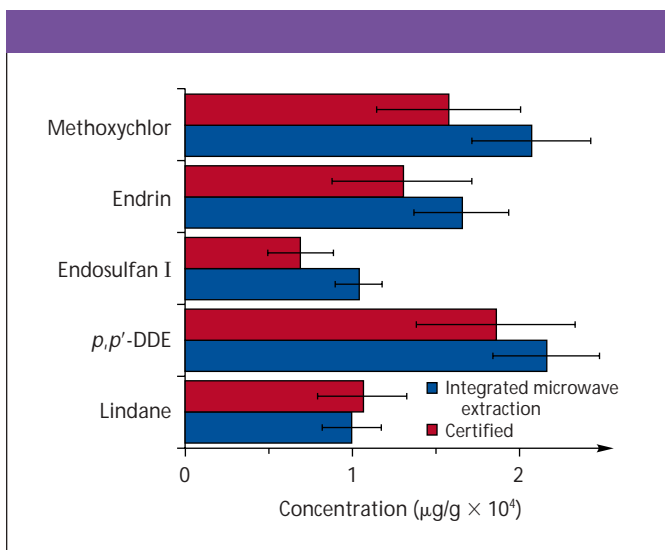
We demonstrated that integrated microwave solvent extraction can be an attractive alternative to traditional solvent extraction techniques. The rapid processing of samples results in significant time savings compared with traditional methods. Feedback real-time computer control of the extraction



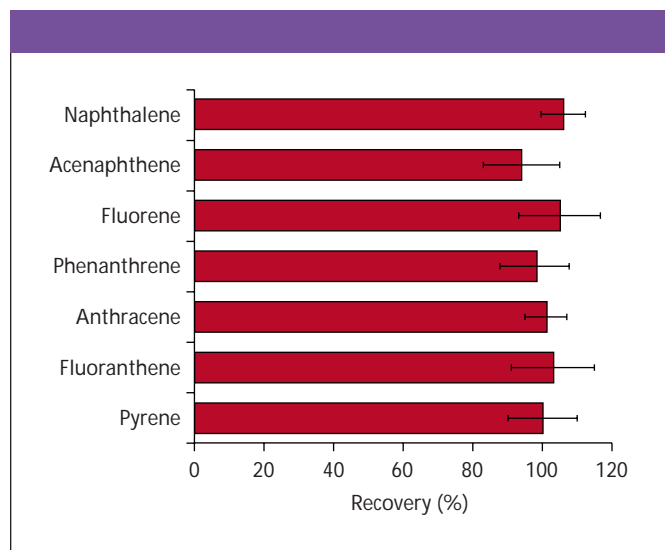
**Figure 3:** Extraction of PAHs using polar solvents. Error expressed as 95% confidence limit ( $n = 6$ ).



**Figure 4:** Extraction of PAHs using nonpolar solvents. Error expressed as 95% confidence limit ( $n = 6$ ).



**Figure 5:** Extraction of organochlorine pesticides. Error expressed as 95% confidence limit ( $n = 4$ ).



**Figure 6:** Evaporation recoveries using hexane. Evaporation solution concentration range: 10–30 µg/mL. Error expressed as 95% confidence limit ( $n = 6$ ).

parameters increases precision and safety of the procedure. The integration of processes ensures enhanced extraction efficiency. The automation of sample processing minimizes sample manipulation, thereby reducing the potential for operator error. A secondary microwave absorber allows the use of nonpolar solvents, which enables analysts to design extraction protocols that optimize the chemistry of the solvent and process.

Although the initial investment for a microwave-assisted solvent extraction system is higher compared with Soxhlet extraction equipment, microwave-assisted solvent extraction systems have lower costs for solvent use and disposal. Analysts also face reduced exposure to hazardous solvents. The consumption of these solvents and their subsequent disposal is substantially reduced, which makes microwave-assisted solvent extraction a more economical and ecologically sound process (Table I). Ongoing work includes mechanistic elucidation

**Table I:** Comparison study for processing 1000 samples

Technique	Time Required (h)	Solvent Consumed (L)
EPA 3540C (Soxhlet)	13,167	450
Integrated microwave extraction	257	15.96*

\*Solvent consumption of integrated microwave extraction was calculated using the outer vessel solvent four times before discarding.

of the process and application to various matrices. This technique has many useful applications, not only in the environmental and pharmaceutical fields, but also in general laboratories that need more-rapid extractions with increased accuracy and precision and an environmentally friendly overall approach.

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