III.b) Frecuencia de modulación de la amplitud

III.b.1) Experimento: Se procedió igual que en los casos anteriores, pero midiéndose el periodo sólo una vez. El experimento se repitió cinco veces, calculándose el valor del período promedio y su correspondiente error relativo.

Valor promedio del período de modulación de la amplitud: $T_{amplitud\ exp.} = (2{,}9 \pm 0{,}1)$ s

Frecuencia angular: $W_{amplitud\ exp.} = (2{,}166 \pm 0{,}07)\ s^{-1}$

III.b.2) El modelo teórico: Dadas las condiciones de trabajo del sistema se calcularon teóricamente los valores correspondientes al período y la frecuencia de modulación de la amplitud, sabiendo que la frecuencia que modula la amplitud es:

$Wamplitud = \frac{W_1 - W_2}{2}$, resultando en este caso $W_{amplitud\ teórica} = (2{,}3 \pm 0{,}1)\ s^{-1}$

El período teórico de modulación de la amplitud es: $T_{amplitud\ teórica} = (2{,}7 \pm 0{,}1)$ s

El error relativo porcentual resultó: $E_{T\ amplitud}\ \% = 7\ \%$. Si bien este valor de error es mayor que en los otros experimentos, dadas las dificultades que se presentaron en la misma para realizar las mediciones, no se lo considera demasiado elevado, por lo que se sigue aceptando que el modelo teórico describe el comportamiento real del sistema físico.

CONCLUSIONES

Se presentaron las actividades desarrolladas por un estudiante avanzado de la carrera de ingeniería química. Las mismas se llevaron a cabo con el objetivo de contrastar un modelo teórico con datos experimentales, de manera de evaluar si dicho modelo es adecuado para describir el comportamiento real de un sistema físico. Se estudió el sistema compuesto por dos osciladores mecánicos acoplados.

Se diseñaron experimentos en los que se tuvieron que tomar precauciones en cuanto a las condiciones de experimentación, no obstante, las mismas son de relativamente fácil reproducción en el laboratorio de física.

Se encontró que las discrepancias entre los resultados experimentales y los obtenidos a partir de cálculos teóricos fueron aceptables en los tres experimentos realizados. Esto permite concluir que el modelo teórico describe adecuadamente el comportamiento real del sistema físico.

Las tareas involucradas en este trabajo, y los criterios adoptados en dicho proceso de validación pueden reproducirse al abordar el estudio de otros sistemas físicos.

Se concluye que el tipo de actividades que se describen en este trabajo, llevadas al aula de física, brindan la oportunidad a los estudiantes no sólo de comprender el papel que juegan los modelos en la construcción del conocimiento científico, sino también su carácter de subordinación al experimento en el marco interpretativo del cuerpo teórico.

La experimentación en física es una actividad de gran valor didáctico, se sostiene que el diseño de actividades en las que aparezca en forma explícita el objetivo de contrastar modelos teóricos con resultados experimentales debería presentarse con mayor frecuencia en los cursos de física universitaria.

AGRADECIMIENTOS

Este trabajo ha sido realizado en el marco de los proyectos: CAID2005/PI 06-32 UNL; PICT 04-13646-BID 1728/OC-AR-UNL; CAID2005/PI 06-31 UNL. Argentina.

Se agradece a la Dra. Sonia Concari por la lectura crítica de esta presentación.

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Received: 5.01.2007 / Approved: 20.04.2008

Solvent free essential oil extraction. A simple and rapid approach to microwave hydrodistillation

Rápida extracción de aceites sin solvente. Un simple acercamiento a la hydrodestilación por microondas

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Abstract

Alternative methods of microwave assisted distillation for use in the extraction of essential oil from citrus fruits have been investigated. Two routes that offer the possibility of significantly enhancing the extraction process are described and their applicability for use within secondary and tertiary level courses has been appraised. The systems take advantage of domestic microwave oven configurations and can be readily adopted using conventional laboratory equipment. No modification of the microwave cavity is required and the processes have been shown to provide a rapid, efficient and, importantly, a solvent free method of extraction.

***Key words**: microwave, essential oil, limonene, extraction, green chemistry*

Resumen

Métodos alternativos de destilación asistida por microondas para el uso en la extracción de aceites esenciales de cítricos han sido investigados. Dos rutas, que ofrecen la posibilidad de realzar considerablemente el proceso de extracción son descritas y su aplicabilidad para el empleo dentro de cursos de segundo y tercer nivel ha sido valorada. El sistema aprovecha las configuraciones de microondas domésticos y fácilmente puede ser adaptado usando el equipo convencional de laboratorio. Ninguna modificación de la cavidad del microondas es requerida y el proceso ha resultado ser rápido, eficiente y lo más importante, un método de extracción sin solvente.

***Palabras clave**: microondas, aceite, extracción, química verde.*

INTRODUCTION

The use of microwave ovens in the chemistry laboratory has increased dramatically in recent years and has successfully emerged from its research origins to commercial application (DA SILVA *et al*., 2006; KAPPE, 2006; Ng *et al.*, 1999; STADLER *et al*., 2003; WOLKENBERG *et al*., 2005). The undergraduate teaching laboratory has largely kept pace with many of the developments in the technology and new experiments can be routinely found within the educational literature. Enhancements to organic preparations (COLEMAN, 2006; FISCHER & FREITAG, 2006; KATRITZKY *et al*., 2006; MONTES *et al*., 2006; MUSIOL *et al*., 2006; ROSSINI *et al*., 2004), sample digestions (FREEMAN & MCCURDY, 1998; GOLTZ *et al*., 2000; SHEFFIELD & NAHIR, 2002; THOMPSON & GHADIALI, 1993) and green chemistry (BAHADIR & KONIG, 2002; DINTZNER *et al*., 2006; ELDER & Holtz, 1996; WHITE & KITTREDGE, 24) demonstrations tend to predominate and effectively mirror advances from the research community. One area where the technology has failed to transfer however lies in the use of microwaves for the extraction of essential oils (DENG *et al*., 2006; FERHAT *et al*., 2006; WANG *et al*., 2006; YE *et al*., 2006). The latter is routinely used within research applications providing significant improvements in extraction time, yield and quality. The latter could prove to be invaluable within both the secondary and tertiary teaching environment where it offers the possibility of commuting the time-consuming distillation step to something that can be achieved within a matter of minutes. The main drawback to the adoption of the technique lies in the fact that the condenser and receiver must lie outwith the oven cavity and has hitherto required substantial modification of the domestic oven found within most teaching laboratories. Health and safety considerations and the possibility of microwave leakage have effectively prevented the adoption of this technique within the educational sector. The present communication has sought to explore a number of avenues through which microwave distillation could be achieved within a conventional oven without compromising the integrity of the shielded oven compartment and hence would retain the necessary health and safety compliance.

The extraction of limonene from citrus fruit was used as the model system given that it represents an established undergraduate experiment from which technique comparisons could easily be drawn (GARNER & GARIBALDI, 1994; WILLIAMS & PIERCE, 1998). This is an important showcase practical with the increasing interest in the chemistries that surround natural product, nutraceutical and aromatherapy health treatments (WANG & WELLER, 2006). The processes of extraction, purification and characterisation have important resonances across a variety of curricula that extend from secondary school to undergraduate and masters level programmes. In principle, it is sufficiently robust to be a candidate for use as a demonstration tool at the secondary level. In practice, steam distillation of the product can be laborious and requires both patience and vigilance on the part of the experimentalist and students will certainly struggle to complete the whole process within an hour. Accommodating the experiment within the more stringent limitations of a secondary school timetable will rarely be possible. The contextual merits of the experiment are clearly significant and, as such, we had sought to explore the possibility of accelerating the extraction stage. Our target was the transformation of the process – preparation to characterisation - such that it should easily be completed within one hour and hence would be suitable for use at the secondary level.

EXPERIMENTAL METHODOLOGY

There should be little surprise in the fact that the rapid heating characteristics of the domestic oven provide an ideal means of generating steam. The condensing component of the distillation process is unfortunately negated by the very same attributes unless it is possible to transfer the steam outwith the oven compartment where it can subsequently condense without being affected by the continued microwave irradiation. A*d hoc* modification of the oven is often necessary to accommodate a Clevenger type collection system as indicated in Figure 1A. The physical breach required to fit the associated quickfit© connector through the top of the oven casing presents the most immediate problem in terms of safety. We examined two alternatives to this approach in which the physical modification of the oven structure could be avoided.

External Condensing System

This first approach is little more than an adaptation of the conventional research system in which the steam is generated within the microwave cavity and subsequently condenses outside the oven. In this instance, narrow bore silicone tubing was used to facilitate the transport of the steam through the existing ventilation holes inherent to the oven design as shown in Figure 1B. Almost all domestic ovens have ventilation holes to allow the

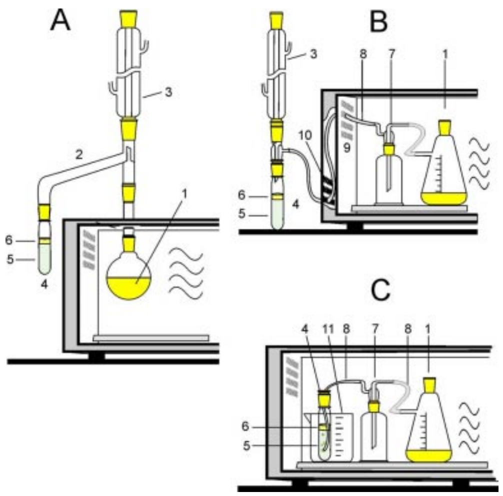

Figure 1. Options available to microwave assisted hydrodistillation. Components: 1. sample vessel; 2. Clevenger side arm; 3. condensor; 4. sample receiver; 5. hydrosol (aqueous) layer; 6. oil layer; 7. foam trap; 8. silicone tubing; 9. internal steam vent; 10. external steam vent; 11. iced receiver container.

escape of steam. These are spatially offset, as indicated in the Figure 1B, such that there is no leakage of microwave radiation. It is therefore possible to exploit this feature as a conduit through which the steam could be transported to an external condenser. The flexibility of the tubing allows it to be threaded neatly through the casing without requiring the mechanical modification of the oven shielding. It is then connected to a standard condenser in much the same way as the Clevenger system but without the need for the side arm. Silicone was used in preference to PVC tubing as the former has a wide temperature stability (>200^{o}C) that ensures that the channel cross section is not altered as a consequence of transporting what will effectively be superheated steam.

Internal Condensing System

Our strategy in this instance has been to develop a process that exploits the differential heating of sample and collection vessels such that the transfer from one to the other can be achieved directly within the oven cavity. This would present a much neater arrangement for the laboratory environment - reducing the complexity of the arrangement whilst possessing a minimal bench footprint. The basic schematic of the *in situ* distillation system is detailed in Figure 1C. There are three distinct components: a sample vessel; a dual entry conical flask that serves as a secondary foam trap and, finally, a collection vessel shrouded with ice and which contained a small quantity of iced water. The receiver is again connected to the trap by means of silicone tubing - the end of which is immersed directly within the ice water.

It could be anticipated that microwave heating would result in the rapid boiling of the sample with the steam carrying the limonene beyond the trap before condensing in the iced water of the receiver. The latter will also start to heat in the course of the experiment but, providing the timescale is sufficiently restricted (less than 5 minutes), should continue to catch the limonene product. If microwave irradiation continues unchecked, then the receiving solution will start to boil and effectively vaporise the product within the receiver - compromising the potential yield.

Sample Preparation

Samples of citrus fruit (orange, lime or grapefruit) were homogenised in a conventional food liquidiser along with 200 mL of deionised water. The resulting suspension was then transferred to a 500 mL Buchner or roundbottom flask and placed within the oven cavity. The flask was subjected to irradiation (800 W) for an appropriate period depending on the approach taken. The extract (oil and hydrosol) was collected in the receiver and then analysed using conventional instrumental (GC-FID, GC-MS, NMR) and bench (tlc) techniques.

RESULTS AND DISCUSSION

In both approaches, the citrus oil was liberated and could be clearly identified within the receiving collection tube as indicated in Figure 2. This could be easily separated without the need for secondary solvent extraction and hence could be considered to be a valuable showcase demonstration for "Green Chemistry" procedures. Gas chromatographic analysis (Figure 3) of the resulting oil is consistent with that extracted by conventional steam distillation methods or solvent extraction.

The oil was extracted after little more than 5 minutes of microwave irradiation with whole process, from sample preparation to extract, easily accomplished within 30 minutes. As such, it allows for an introductory explanation and the subsequent characterisation of the product within a conventional laboratory practical session. The main difference between the two approaches detailed in Figures 1B and 1C relates to the amount of material that can be extracted. The external condensing system allows prolonged extraction and hence a more significant yield of oil. The power output of the oven must be lowered after the flask has begun to boil to prevent excessive frothing and carry over of the plant material into the receiver. The latter can be prevented by the addition of small external trap prior to the steam reaching the condenser.

The yield attainable from the *in situ* configuration, in contrast, is limited to the time taken for the iced receiver to melt. In the experiments detailed above - whole fruit extraction was used and it is likely that the yield of oil will vary depending on fruit variety, age and the intensity and duration of the irradiation. Given the peel from a common orange cultivar - 0.07 g of oil per g of peel could typically be extracted using a domestic 800 W oven operating over a period of 5 minutes. The percentage recovery of limonene (based on 0.5 g of the commercial product spiked into 100mL deionised water) was 40% - again for a typical 5 minute irradiation period. The recovery can obviously be improved by the use of consecutive ice receivers but, for normal teaching purposes, the quantities attainable in a single run are generally sufficient for a host of follow up experiments whether classical or instrumentation based.

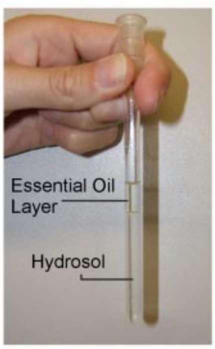

Figure 2. Example extract (orange oil) highlighting the separation of oil and aqueous layers.

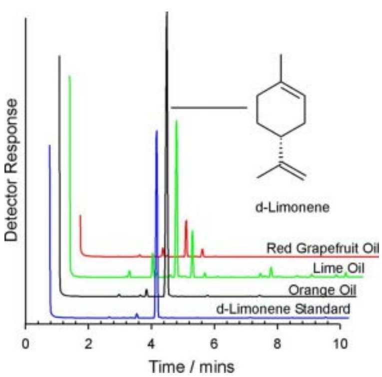

Figure 3. GC-FID analysis of citrus oil obtained through microwave extraction and comparison with a commercial limonene standard.

CONCLUSIONS

There is little doubt that microwave assisted distillation can facilitate the rapid and efficient extraction of plant oils. The approaches investigated in this communication have shown how the techniques can be readily adapted for use within both the secondary and tertiary sectors with minimal technical requirements beyond those available within the traditional laboratory environment. The integrity of the oven housing is retained and presents no safety risk to staff or students beyond the normal COSHH regulations. The techniques have been demonstrated with a variety of citrus oil systems and have shown that solvent free isolation can easily accommodated - as either a hands on practical or showcase demonstration - within ever restrictive timetabling. The techniques are generic and could readily be applied to other plant material and offer a versatile route through which to adapt or extend the process to fit the requirements of particular courses and curricula.

ACKNOWLEDGEMENTS

The authors wish to thank the Royal Society for financial support in the development of the technique.

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